HONI SOIT QUI MAL Y PENSE
DIEU ET MON DROIT

Agricultural Research Institute
PUSA

The Journal
of
Physical Chemistry

Published under the auspices of the American Chemical
Society, the Chemical Society, and the Faraday Society

Editor
Wilder D. Bancroft

Associate Editors

A. L. Day	T. M. Lowry
F. G. Donnan	J. W. McBain
G. A. Hulett	W. L. Miller
I. Langmuir	J. C. Philip

VOLUME XXX

ITHACA, N. Y.
THE EDITOR

1926

CONTENTS OF VOLUME XXX

1. JANUARY

Jean Oliver and Pearl Smith,	The Kinetics of Agglutination of Red Blood Cell Suspensions,	1
F. W. Bergstrom,	Reaction of the Type $Cl_2+2KOH=KCl+KClO+H_2O$,	12
H. B. Weiser,	The Antagonistic Action of Ions in the Neutralization of Sols,	20
A. L. Marshall,	Photosensitization by Optically Excited Mercury Atoms. The Hydrogen Oxygen Reaction,	34
G. S. Parks and K. K. Kelley,	The Heat Capacities of Some Metallic Oxides,	47
W. R. Brode,	The Effect of Solvents on the Absorption Spectrum of a Simple Azo Dye,	56
A. R. Collett and John Johnston,	Solubility Relations of Isomeric Organic Compounds. VI,	70
Charles Gurchot,	Reversible Permeability of Membranes and its Relation to Cell Metabolism,	83
W. A. Rudisill and C. J. Engelder,	Catalytic Activation of Titania,	106
J. W. McBain and D. G. Hopkins,	Films of Adhesives,	114
Victor Lenher and C. H. Kao,	Studies on the Chemistry of Gold,	126
B. H. Carroll,	The Photochemical Oxidation of Leuco Bases,	130
W. A. Patrick and P. W. Bachman,	The Adsorption of Ions on a Mercury Surface,	134
New Books		136

2. FEBRUARY

H. S. Taylor,	Fourth Report of the Committee on Contact Catalysis,	145
L. A. Munro and F. M. G. Johnson,	The Sorption of Vapors by Alumina,	172
O. K. Rice,	Equilibrium in Colloid Systems,	189
L. M. Currie,	Antimony Sulphides,	205
J. W. McBain,	The Apparent Viscosity of Colloidal Solutions and a Theory of Neutral Colloids as Solvated Micelles capable of Aggregation,	239
S. B. Hendricks,	Equilibrium in the System: Arsenic Pentoxide, Barium Oxide, Water,	248
F. Hardy,	Anomalous Flocculation in Colloidal Clays and Soils,	254
F. H. Getman,	The Ultraviolet Absorption Spectra of Aqueous Solutions of Sulphur Dioxide and some of its Derivatives,	266
N. R. Dhar,	Origin of the Formation of Deposits in Gout and Other Diseases, and the Cause of Swelling in Beriberi,	277
New Books		282

3. MARCH

W. Mund and W. Koch,	The Chemical Action of Alpha Particles on Acetylene,	289
S. Ghosh and N R. Dhar,	The Influence of Ions carrying the Same Charge as the Dispersed Particles in the Inversion of Emulsions,	294
W. C. Arsem,	Gel Structure,	306
J. W. McBain, C. E. Harvey and L. E. Smith,	The Apparent Viscosity of Solutions of Nitro Cotton in Various Solvents,	312
W. A. Lazier and Homer Adkins,	Adsorption of Ethylene and Hydrogen by Zinc Oxide, Iron Oxide, Nickel, and Copper,	353
R. W. Harman,	Aqueous Solutions of Sodium Silicates. II,	359
A. F. O. Germann and H. S. Booth,	Thermal Analysis of the System Boron Trifluoride-Hydrogen Sulphide,	369
N. R. Dhar,	Old Age and Death from a Chemical Point of View	378
C. W. Mason,	Structural Colors in Insects. I,	383
J. T. Burt-Gerrans,	The Electrolysis of Acid Solutions of Copper Sulphate. II,	396
R. B. Mason and J. H. Mathews,	The Effect of Ultra-Violet Light on the Oxidation of Sodium Sulphite by Atmospheric Oxygen,	414
New Books		421

4. APRIL

H. S. Harned,	Individual Thermodynamic Behaviors of Ions in Concentrated Solutions including a Discussion of the Thermodynamic Method of computing Liquid-Junction Potentials,	433
R. O. Herzog,	The Nature of the Structure of Cellulose and its Significance in Chemical Transformations,	457
W. L. Nelson and C. J. Engelder,	The Thermal Decomposition of Formic Acid,	470
B. B. Wescott and C. J. Engelder,	The Catalytic Decomposition of Formic Acid,	476
N. R. Dhar,	Influence of Temperature on Metabolism and the Problem of Acclimatization,	480
M. L. Nichols and I. A. Derbigny,	The Reduction of Nitrous Oxide,	491
T. E. Phipps and W. R. Brode,	A Comparative Study of Two Kinds of Colored Rock Salt,	507
Wilder D. Bancroft,	Blue Wood,	521
C. H. Kunsman,	The Thermionic Properties of Some Mixtures used as Catalysts in the Synthesis of Ammonia,	525
V. R. Main,	The Viscosity of Aqueous Solutions of the Silicates of Soda,	535
W. W. Lucasse,	The Transference Numbers of Hydrochloric Acid in Glycerol-Water Mixtures,	562
New Books		566

5. MAY

A. F. Scott,	A Relationship between Atomic Numbers and the Properties of Ions in the Crystal Lattice. II,	577
H. V. Tartar and M. F. Perkins,	A Laboratory Study of Nitrogen Fixation in the High Tension Arc,	595

J. B. Firth and W. L. Purse, Organogels of Silicic Acid—the Replacement of the Water in the Hydrogel by Alcohol, 617
S. B. Arenson, P. E. Roller and D. J. Brown, The Reactive Nature of Aldehydes from the Standpoint of the Apparent Electromotive Force, 620
N. R. Dhar and S. Ghosh, Studies in Adsorption. XIII, 628
Isaac Bencowitz and H. T. Hotchkiss, Jr., Vapor Pressure Lowering as a Function of the Degree of Saturation. II, 643
R. M. Woodman, The Preparation and Conditions of Formation of the Two Possible Types of Emulsion in the System Cresylic Acid—Gelatine—Water, 658
D. H. Peacock, The Benzylation of Amines. III, 673
B. Bruzs, Velocity of Thermal Decomposition of Carbonates, 680
F. S. Brown and C. R. Bury, Cryoscopic Measurements with Nitrobenzene. IV, 694
P. B. Ganguly, The Scattering of Light by Aqueous Sodium Silicate Solutions, 706
Hsi-Ching Chen, A Laboratory Latex, 713
New Books 716

6. JUNE

N. L. Bowen, Properties of Ammonium Nitrate. I, 721
N. L. Bowen, Properties of Ammonium Nitrate. II, 726
N. L. Bowen, Properties of Ammonium Nitrate. III, 736
F. F. Sherwood and E. I. Fulmer, The Effect of Temperature upon the Growth of Yeast in Various Media, 738
A. L. Marshall, Mechanism of the Photochemical Reaction between Hydrogen and Chlorine. III, 757
H. V. Tartar and C. Z. Draves, A Study of the Precipitation of Mastic Suspensoids, 763
J. N. Brönsted, The Acid-Basic Function of Molecules and its Dependency on the Electric Charge Type, 777
J. R. Pound, Interfacial Tensions between Organic Liquids and Water or Aqueous Solutions, 791
C. F. Fryling, Heats of Adsorption and the Problem of Promotor Action, 818
S. Ghosh and N. R. Dhar, Studies in Adsorption. XIV, 830
M. C. Hylan, Grain Size and the Quantum Theory of Photographic Exposure, 845
G. McP. Smith, Ionic Activity versus Concentration in the Interpretation of Equilibria between Amalgams and Aqueous Sodium and Potassium Halide Mixtures, 849
New Books 858

7. JULY

H. F. Vieweg, Frictional Electricity, 865
W. Mund, Ionization by Radon in Spherical Vessels, 890
W. A. Lazier and Homer Adkins, The Formation of Carbon Dioxide from Alcohols, 895
R. C. Cantelo, The Thermal Decomposition of Methane. II, 899
H. B. Oakley, The Origin of the Charge on Colloidal Particles, 902
R. W. Harman, Aqueous Solutions of Sodium Silicates. III, 917

J. P. McHutchison, The Electrodeposition of Radium D and Radium E, 925
W. W. Lucasse and J. McA. Harris, Jr., The Transition Points of Salt Hydrates in Non-aqueous Solutions, 930
C. C. Palit and N. R. Dhar, Catalytic and Induced Oxidation of Some Carbohydrates, Uric Acid, and Inorganic Substances, 939
F. L. Usher, Electrokinetic Behavior and Electrode Potential, 954
H. C. Howard, Jr., Mechanism of the Catalytic Dehydration of Methanol, and Some Properties of the Hydrous Aluminum Oxide Catalyst, 964
R. H. Lambert, The Ternary System: Silver Bromide—Potassium Bromide—Water, 973
W. H. Hampton, The Potential of the Iron Electrode, 980
A. J. Stamm and E. O. Kraemer, A Note on the Mechanism of Emulsification, 992
New Books 1001

8. AUGUST

A. F. Sco , A Relationship between Atomic Number and the Properties of Ions in the Crystal Lattice, 1009
E. J. Miller, Adsorption from Solution by Ash-free Charcoals. I, 1031
H. A. Neville, Adsorption and Reaction. I, 1037
A. W. Laubengayer and R. B. Corey, Germanium. XIII, 1043
A W. Laubengayer and D. L. Tabern, Germanium. XIV, 1047
L. M. Dennis, W. R. Orndorff and D. L. Tabern, Germanium. XV, 1049
L M. Dennis and F. E. Hance, Germanium. XVI, 1055
H. S. Harned and G. M. James, The Dissociation of Water in Potassium and Sodium Bromide Solutions, 1060
E. Posnjak, The Nature of Stannic Acids, 1073
A. L. Marshall, The Mechanism of Reactions photosensitized by Mercury Vapor, 1078
R. W. Harman, Aqueous Solutions of Sodium Silicates. IV, 1100
J. P. McHutchison, Experiments on the Electrolysis of Radium D and Radium E, 1112
M. L. Byron, The Peptization of Pyroxylin, 1116
C. C. Palit and N. R. Dhar, Action of Nitric Acid on Metals in presence o Catalysts, 1125
R. E. Burk, A Possible Mechanism for the Lowering of the Heat of Activation of a Reaction by a Catalytic Surface, 1134
New Books 1141

9. SEPTEMBER

O. E. Frivold, The Influence of the Ionic Charge on the Osmotic Behavior of Alcoholic Solutions, 1153
E. J. Miller, Adsorption from Solution by Ash-free Adsorbent Charcoals. II, 1162
J. W. Williams and J. A. Skogstrom, Colloidal Systems of Nitromethane, 1170
G. S. Parks and K. K. Kelly, The Heat Capacity of Calcium Silicate, 1175
Simon Klosky and Leo Woo, Solubility of Silver Oxide, 1179
H. A. Neville, Adsorption and Reaction. II, 1181
M. R. Mehrotra and N. R. Dhar, Studies in Adsorption. XV, 1185

Wilder D. Bancroft, The Water Equilibrium, 1194
John McAulay, Jr., Influence on the Solubilities of Salts in Water by the Addition of a Non-electrolyte to the Solution, 1202
H. J. M. Creighton, Solubility and Electrolytic Conductance of Mesitylene Phosphinous Acid, 1209
H. B. Dunnicliff, I. S. Sikka and R. C. Hoon, The System: Sodium Sulphate, Sulphuric Acid, Ethyl Alcohol, 1211
O. W. Richards, A Nomogram for the van't Hoff-Arrhenius Temperature Equation, 1219
E. J. Joss, The Action of Metals on Nitric Acid, 1222
F. M. Cray, The Color Change of Congo Red in Acidified Acetone-Water Solutions, 1276
R. M. Woodman, The System: Water, Acetic Acid, Toluene, 1283
New Books 1287

10. OCTOBER

Shun-ichi Uchida, On the Reaction Mechanism of the Catalytic Oxidation of Ammonia, 1297
J. E. Rosenberg and Gebhard Stegeman, The Adsorption of Ions by Metallic Mercury, 1306
H. Lee Ward, The Solubility Relations of Naphthalene, 1316
William Rogers, Jr. and H. S. Taylor, The Rate of Oxidation of Linseed Oil, 1334
O. K. Rice, The Surface Tension of Charged Surfaces, 1348
G. B. Kistiakowsky, The Ionisation Potentials of Nitrogen and Hydrogen on Iron and Other Metals, 1356
K. Kawamura, Adsorption by Humic Acid, 1364
J. H. Yoe and E. B. Freyer, The Effect of Hydrogen Ion Concentration on the Viscosity of Hydrosols of Aluminum, Chromic and Ferric Oxides, 1389
Maud Garner and W. C. McC. Lewis, The Effect of Temperature on the Rate of Coagulation of Gold Sol, 1401
Maud Garner, Note on the Significance of the Variation in the Smoluchowski Coagulation Coefficient (β), 1410
A. F. Benton, A Gel of Metallic Platinum, 1415
H. A. H. Pray, The Stability of Diazo-Benzene Chloride Solution. I, 1417
P. W. Cunliffe, R. G. Franklin, R. E. W. Maddison, and L. Reeve, Studies in Photochemical Technique. III, 1427
New Books 1432

11. NOVEMBER

C. W. Stillwell, The Color of the Ruby, 1441
E. C. H. Davies and Victorian Sivertz, Rhythmic Diurnal Bands of Gold and Platinum in Silicic Acid Gel, 1467
H. A. H. Pray, The Stability of Diazo-Benzene Chloride Solutions. II, 1477
A. F. Benton and T. L. Williams, The Catalytic Oxidation of Carbon Monoxide in Contact with Quartz Glass, 1487
Mary R. Andrews, Vapor Pressure of Naphthalene at Low Temperatures, 1497

O. K. Rice,	A Study of the Electrocapillary Curve near its Maximum,	1501
L. M. Dennis and A. W. Laubengayer,	Germanium. XVII,	1510
H. B. Weiser,	The Antagonistic Action of Ions in the Neutralization of Sols,	1527
R. A. Beebe,	Heat of Adsorption of Carbon Monoxide on Copper Catalyst,	1538
J. W. McBain and M. C. Field,	The Equilibrium underlying the Soap-boiling Process. The System Potassium Laurate-Potassium Chloride-Water,	1545
S. Ghosh	Influence of Ageing of a Sol on its Coagulation,	1564
New Books		1571

12. DECEMBER

Gösta Åkerlof,	The Solubility of Strong, Simple Electrolytes in Water,	1585
A. A. Groening and H. P. Cady,	Decomposition Potentials and Metal Overvoltages in Liquid Ammonia and Water,	1597
M. Bergstein and Martin Kilpatrick, Jr.,	The Catalytic Minimum Point,	1616
L. H. Reyerson, O. E. Harder and L. E. Swearingen,	The Nature of Metal Films reduced on the Surfaces of Silica Gel,	1623
G. S. Forbes and P. A. Leighton,	Electrolysis of Dichromic Acid under a Mercury Vapor Lamp of High Intensity,	1628
A. L. Marshall,	Synthetic Formaldehyde from Carbon Monoxide and Hydrogen,	1634
R. C. Cantelo,	The Methane Equilibrium. I,	1641
D. N. Chakravarti and N. R. Dhar,	Viscosity Measurements of Certain Sols in presence of Electrolytes,	1646
O. K. Rice,	Equilibrium in Colloid Systems. II,	1660
J. C. W. Frazer, B. F. Lovelace and R. K. Taylor,	The Vapor Pressures of Potassium Nitrate Solutions at 20° C,	1669
J. N. Pearce and M. M. Hicks,	A Sensitive Electrical Precision Apparatus for the Determination of the Boiling Point Elevation,	1678
Wilhelm Stenström and Norris Goldsmith,	Determination of the Dissociation Constants of Phenol and the Hydroxyl Group of Tyrosine by means of Absorption Measurements in the Ultra-violet,	1683
J. F. King and R. N. Washburne,	The Electromotive Determination of Small Amounts of Ferric Iron,	1688
Name Index		1698
Index to New Books		1704
Subject Index		1706

THE KINETICS OF AGGLUTINATION OF RED BLOOD CELL SUSPENSIONS*

BY JEAN OLIVER AND PEARL SMITH

In a study of the action of electrolytes on the electric charges and stability of red blood cell suspensions Oliver and Barnard[1] have shown that at a certain concentration of trivalent salts agglutination of the cells proceeds at a maximum speed. It was also observed that at this concentration the electric charge of the cells was completely abolished, whereas in other concentrations where the charge had been only depressed below the critical potential, agglutination, although it occurred, was much slower (Fig. 1). It was therefore suggested that the conditions were analogous to those described by Zsigmondy in the coagulation of colloidal solutions by electrolytes.

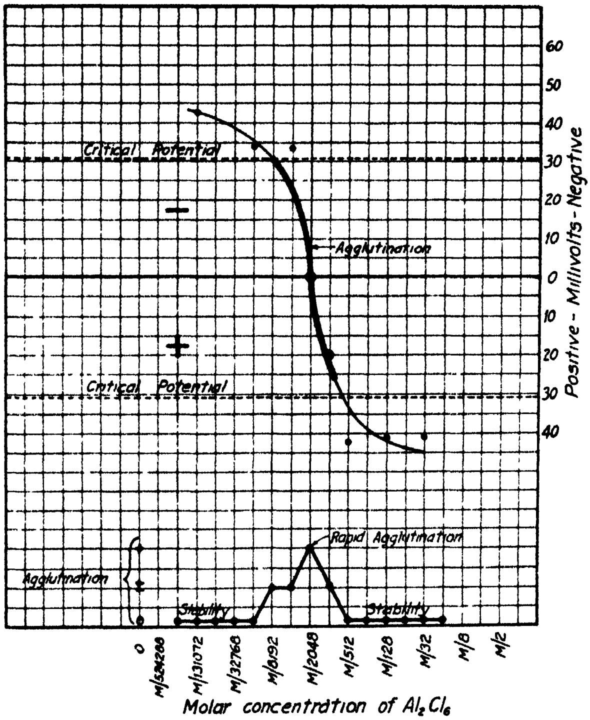


FIG. 1

In his experiments with colloidal gold Zsigmondy[2] found that the time of color change at first decreased rapidly and then became constant as the concentration of the coagulating electrolyte was increased and this range of concentration in which the color change was constant he called the zone of "rapid" coagulation. By comparing his measurements with those of Galecki[1] on the cataphoresis of similar particles he assumed that this zone of rapid coagulation lay in the immediate neighborhood of the isoelectric point, and was the result of the complete neutralization of the charge of the particles.

---

*From the Department of Pathology of the Medical School of Stanford University, San Francisco, California.

[1] J. Gen. Physiol. 7, 99 (1924).

[2] Z. physik. Chem. 92, 600 (1917).

These experiments of Zsigmondy formed the starting point for the development of a theory of coagulation. He assumed that in the rapid coagulation of spherical particles of equal size, any particle which comes within a certain distance of another particle becomes permanently fixed to it since it possesses no electric charge to cause repulsion. This distance he defined as the radius of the attraction sphere of the particle.

The mathematical treatment of the problem was developed by v. Smoluchowski[2] who calculated formulae for the number of single, double, treble and larger aggregates in a suspension from (1) the original number of particles (V_o), (2) the radius of the attraction sphere (R), and (3) the velocity constant of Brownian movement (D).

Von Smoluchowski first calculated the probability that any particle will enter the attraction sphere of a given particle by applying the equation for Brownian movement and also the probability that within the time T no particle will enter such an attraction sphere. From these probabilities he calculated the decrease in number of the single particles. By making corrections for the Brownian movements of the particles around which coagulation is supposed to take place, and from the fact that the aggregates already formed act as coagulating nuclei he finally arrived at the following system of equations:

$$V_1 + V_2 + V_3 + \ldots\ldots\ldots \Sigma_v = \frac{V_o}{1 + t/T} \qquad (1)$$

$$V_1 = \frac{V_o}{(1 + t/T)^2} \qquad (2)$$

$$V_2 = \frac{V_o\, t/T}{(1 + t/T)^3} \qquad (3)$$

$$V_K = \frac{V_o\, (t/T)^{K-1}}{(1 + t/T)^{K+1}} \qquad (4)$$

where Σ_v = total number of particles; V_1 = number of single particles; V_2 = number of double particles; $T = 1/4\pi DRV_o$

Von Smoluchowski's theory has been verified by a number of experiments. Zsigmondy[3] first tested the equation $V_1 = V_o / (1 + t/T)^2$ by measuring the decrease in the number of single particles in a gold sol. He was able with the ultramicroscope to distinguish between the single particles and aggregates because the former emit green and the latter yellow light. By substituting the actual values in the equation he obtained a value for $1/T$ which was fairly constant for all but the shorter periods of time. With the average value for $1/T$ he calculated the theorectical values of V_1 for the various time intervals, and found that they agreed approximately with the experimental figures. With the same data, he obtained values between 2.0 and 3.0 for the ratio between the radius of the attraction sphere and the radius of the particle by applying the formula $T = 1/4\pi DRV_0$ in which the value of D was substituted, giving $R/r = N\ 3\eta/H\Theta 2V_0 \cdot 1/T$,* Westgren and Reitstötter[1] studied the change in the total number of particles in gold sols and found that their results were in accord with the equation $\Sigma_v = V_0/(1 + t/T)$, where $H = 8.31 \times 10^7$, gas constant; $N = 6.06 \times 10^{23}$; Avogadro's constant; $\eta = 009$, viscosity of medium; Θ = absolute temperature

---

[1] Z. anorg. Chem. 74, 199 (1912).

[2] Z. physik. Chem. 92, 129 (1917).

[3] Z. physik. Chem. 92, 600 (1917).

Luers[2] has found v. Smoluchowski's formulae applicable to the change of color of Congo red hydrosols when mixed with an electrolyte.

Somewhat divergent results were obtained by Kruyt and van Arkel[3] in their experiments with selenium hydrosols. In several of their experiments, the total number of particles was found to decrease in a way not consistent with v. Smoluchowski's formula. When an agreement with the theory did occur, R/r varied from 0.5 to 1.0.

The formula $\Sigma_v = V_0/(1 + t/T)$ was found by Ehringhaus and Wintgen[4] to apply in experiments with a very different sort of material. In a flux of borax and gold chloride, the particles of gold were found to decrease according to the formula when heated at a temperature of 925 C. for 1 to 500 minutes. In all but one of their series the average value of R/r was 2.39; in one series it was 13.7

In the present investigation an attempt was made to apply v. Smoluchowski's formulae to the "rapid agglutination" of red blood corpuscles.

Methods

In all of our experiments a 1.5 per cent. suspension of red blood cells in 8.5 per cent. sucrose solution was used. In the preparation of the cells fresh defibrinated rabbit blood was washed three times with 0.9 per cent. NaCl solution and three times with 8.5 per cent. sucrose solution. To highly charge and stabilize the suspension sufficient NaOH was added to made a M/500 solution of the hydroxide, and enough Al_2Cl_6 was then added to this mixture to make the concentration of the electrolyte approximately M/4000. This concentration previous experimentation had shown brings the cells of such a suspension to the isoelectric point and produces "rapid agglutination". (Fig. 1).

---

[1] Z. physik. Chem. **92**, 750 (1917).

[2] Kolloid-Z., **27**, 123 (1920).

[3] Rev. Trav. chim., **39**, 656; **40**, 916 (1920).

[4] Z. physik. Chem. **104**, 301 (1923).

At varying intervals the process of agglutination was interrupted by pipetting 2 ccm. of the mixture into a test tube containing 1.0 cm. of a 1.0 per cent. gelatin solution. The progress of agglutination was followed by making counts of single cells or aggregates of cells from each tube. In each case at least three counts were made on the undiluted suspension, using an ordinary blood counting chamber.

SERIES I

Table I—Exp. II

Secs.	$V_1 \times 10^{-6}$ Obs	β	$V^1 \times 10^{-6}$ Calc	$\frac{R}{r}$
0	60.00	—	—	
30	3.15	.1131	3.42	
60	1.30	.0973	1.10	
90	.50	.1115	.53	
	Av.	.1071		598.6

Table IV—Exp. XII

Secs.	$V_1 \times 10^{-6}$ Obs.	β	$V_1 \times 10^{-6}$ Calc.	$\frac{R}{r}$
0	33.20	—	—	
30	2.85	(.08041)	—	
60	1.60	.05925	1.89	
90	1.00	.05291	.99	
120	.75	.04711	.61	
	Av.	.05309		542.5

Table II—Exp. III

Secs.	$V_1 \times 10^{-6}$ Obs	β	$V_1 \times 10^{-6}$ Calc	$\frac{R}{r}$
0	45.15	—	—	
30	5.50	.0618	6.78	
60	2.55	.0534	2.60	
90	1.65	.0470	1.37	
120	.90	.0506	90	
180	.40	.0527	.40	
240	.25	.0605	.25	
	Av.	.0527		396.0

Table V—Exp. XI

Secs.	$V_1 \times 10^{-6}$ Obs	β	$V_1 \times 10^{-6}$ Calc	$\frac{R}{r}$
0	46.40	—	—	
30	7.45	.0498	8.52	
60	2.75	.0518	3.45	
90	2.35	.0382	1.85	
120	1.60	.0365	1.16	
150	.75	.0458	.77	
	Av.	.0445		325.3

Table III—Exp. XIII

Secs.	$V_1 \times 10^{-6}$ Obs	β	$V_1 \times 10^{-6}$ Calc	$\frac{R}{r}$
0	37.40	—	—	
30	12.25	(.0249)	—	
60	7.45	.0207	8.71	
90	6.60	.0153	5.49	
120	4.35	.0165	3.78	
150	2.45	.0194	2.76	
	Av.	.0179		163.0

The Experiments

In Series I single cells only were counted. Fig. 2 shows the manner in which the number of single cells decreases with time; the logarithms of the number of cells per ccm. are used as ordinates and time in seconds as abscissae. In the Tables I-V the constant 1/T or β was calculated from the formula $\beta = 1/T\left(\sqrt{\frac{V_0}{V_1}} - 1\right)$. The calculated values for the number of single cells were obtained by applying the formula $V_1 = V_0/(1 + \beta t)^2$. In each case the β used is the average for the experiment with the exclusion of those enclosed by brackets. These are omitted as obviously too large, since it is impossible to stop the progress of agglutination promptly at this point. The same difficulty was observed by Zsigmondy and others who worked with colloidal solutions. The β for each experiment is fairly constant and the calculated numbers of single cells agree approximately with the actual counts.

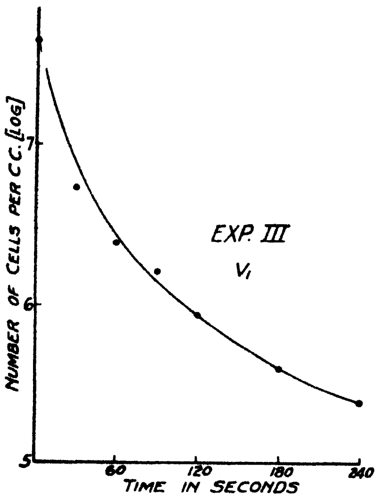


FIG. 2

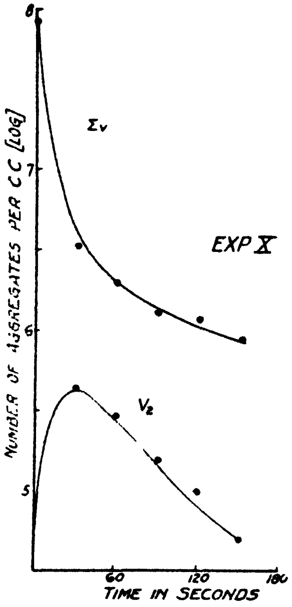


FIG. 3

SERIES II

Table VI—Exp. IX

Secs.	$\Sigma v \times 10^{-5}$ Obs.	β	$\Sigma v \times 10^{-6}$ Calc.	$\frac{R}{r}$
0	22.60	—	—	
30	4.70	(.1273)	—	
60	3.80	.0826	4.03	
90	2.65	.0838	2.86	
120	2.60	.0627	2.21	
		Av. .0769		1152.0

Table VII—Exp. X

0	84.10	—	—	
30	3.35	(.803)	—	
60	2.45	.631	2.17	
90	1.35	.681	1.47	
120	1.25	.551	1.11	
150	.90	.630	.89	
		Av. .623		2513.0

Table VIII—Exp. VI

0	29.10	—	—	
30	4.50	.1820	5.24	
60	2.20	.2040	2.88	
90	1.85	.1670	2.03	
120	1.50	.1530	1.52	
150	1.70	.1073	1.23	
180	1.60	.0955	1.03	
		Av. .1516		1832.0

In Series II the total number of cells and aggregates was counted and similar calculations made with the formulae

$$\beta = 1/t \cdot V_0/\Sigma_v - 1$$

and

$$\Sigma_v = V_0/1 + \beta t$$

Tables VI-VIII and the upper curve in Fig. 3 illustrate experiments of this type. Agreement between the theoretical and observed values is not as close as observed in Series I, but is approximate.

SERIES III

Table IX—Exp. XII

Secs.	$V_2 \times 10^{-6}$ Obs.	β	$V_2 \times 10^{-6}$ Calc.	$\frac{R}{r}$
0	.00	—	—	
30	.80	(.162)	—	
60	.50	.110	.571	
90	.30	.099	.294	
120	.20	.094	.178	
		Av. .101		1032.0

Table XII—Exp. IX

Secs.	$V_2 \times 10^{-6}$ Obs.	β	$V_2 \times 10^{-6}$ Calc.	$\frac{R}{r}$
0	.00	—	—	
30	.85	(.120)	—	
60	.60	.076	.62	
90	.35	.072	.33	
120	.35	.074	.21	
		Av. .074		1108.0

Table X—Exp. XI

0	.00	—	—	
30	1.60	.127	2.20	
60	.70	.110	.82	
90	.50	.090	.42	
120	.40	.077	.26	
150	.20	.092	.17	
		Av. .099		723.8

Table XIII—Exp. XIII

0	.00	—	—	
30	1.90	(.095)	—	
60	1.30	.063	1.64	
90	1.00	.051	.93	
120	.65	.050	.60	
150	.50	.047	.42	
		Av. .053		478.9

Table XI—Exp. X

0	0.0		—	
30	0.45	(.408)	—	
60	0.30	.253	.31	
90	.15	.246	.15	
120	.10	.228	.09	
150	.05	.265	.06	
		Av. .248		1001.0

TABLE XIV

Valves of β obtained in same experiment by different methods.

Exp.	From Σv		From V_1		From V_2	
	β	R/r	β	R/r	β	R/r
VIII	.046	345.2	.0269	206.3	—	
IX	.0769	1152.0	—		.074	1108.0
X	.623	2513.0	—		.246	1001.0
XI	—		.0445	325.3	.099	723.8
XII	—		.0531	542.5	.101	1032.0
XIII	—		.0179	163.0	.0528	478.9

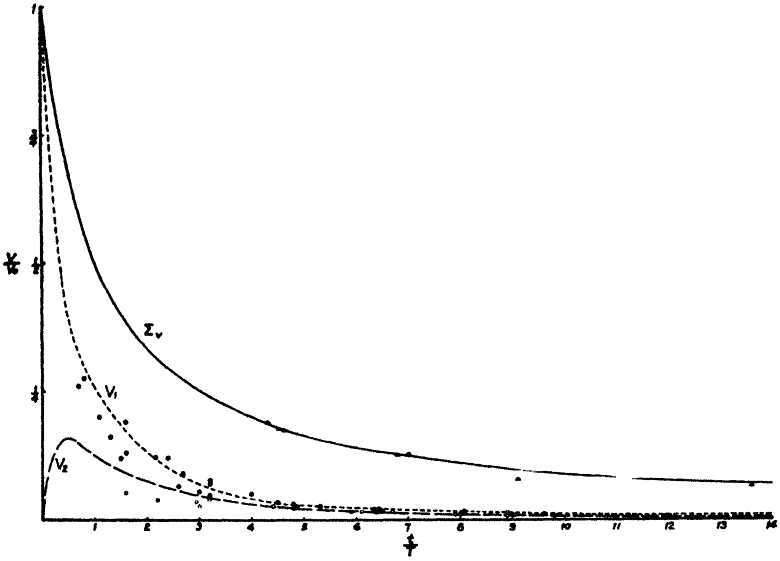


FIG. 4

In Series III, two-celled aggregates were counted and calculations of the values of β and of V_2 made by the use of the equation,

$$V_2 = V_0\,\beta t/(1 + \beta t)^3.$$

The data obtained are shown in Tables IX-XIII, and the type of curve is illustrated by the lower curve in Fig. 3.

In Series IV two different kinds of counts were made from each tube to see if the values for β would be the same for the two counts. There is considerable variation in the β of some of the experiments as is shown by Table XIV. In others the agreement is as satisfactory as can be expected in such a rigorous test of the theory.

Two methods have been devised to give a graphic comparison between the theoretical and experimental values. Von Smoluchowski constructed curves showing the theoretical progress of coagulation based on equations (1) to (4) using v/v° as ordinates and t/T as abscissae. Such a set of theoretical curves, together with the experimental data is shown in Fig. 4.

The second method in which the theoretical values are represented by straight lines was used by Ehringhaus and Wintgen[1]. By the rearrangement of the equation $\Sigma_v = \frac{V_o}{1 + t/T}$ the equation $1/\Sigma_v = 1/V_o + \left(\frac{1/T}{V_o}\right)t$ is obtained and since $1/V_o + \frac{1/T}{V_o}$ is constant for a given experiment, plotting $1/\Sigma_v$ against t should give a straight line. The results are shown in Figs. 5-7.

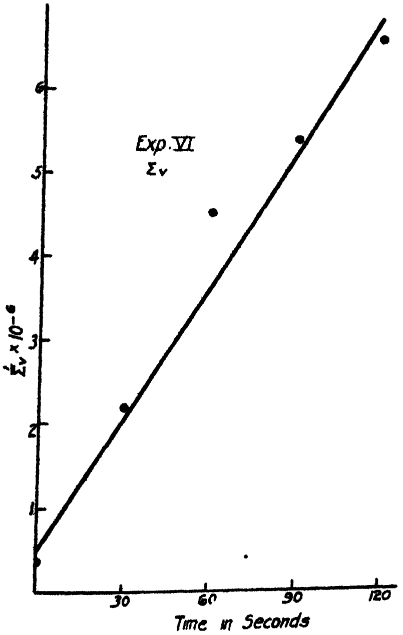


FIG. 5

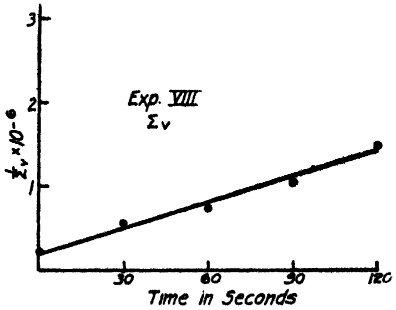


FIG. 6

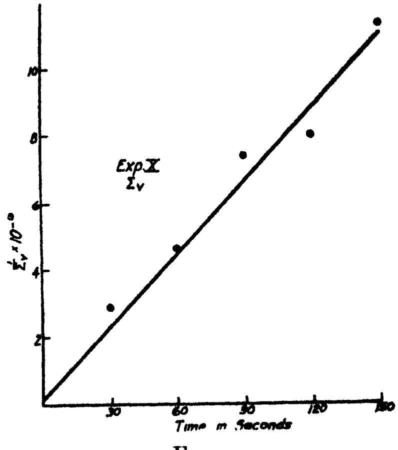


FIG. 7

Similarly the equation $V_1 = \frac{V_o}{(1 + t/T)^2}$ was rearranged, giving $\sqrt{\frac{1}{V_1}} = \frac{1}{\sqrt{V^o}} + \left(\frac{1/T}{\sqrt{V_o}}\right)t$ and $\sqrt{\frac{1}{V_1}}$ plotted against t. .The results are illustrated by Figs. 8-10. Considering the difficulties of the experiment the agreements between the theoretical and observed values are quite satisfactory.

Discussion

Certain differences between the mechanism of chemical reactions and of coagulation have been pointed out by v. Smoluchowski. In chemical union only a definite number of atoms or atom groups unite to form a molecule while in coagulation successive complexes are formed whose size has theoretically no limit. In Figures 11 and 2 the usual kinetic formulae of chemical reactions are applied to the observed rate of agglutinations as expressed by the decrease in the number of single particles, the concentration V_1 being plotted as log V_1 (Fig. 2), and $1/V_1$ and $1/V_1^2$ (Fig. 11). It is seen that the process of agglutination does not follow the course of a mono-, bi- or trimolecular reaction.

---

[1] Z. physik. Chem. 104, 301 (1923).

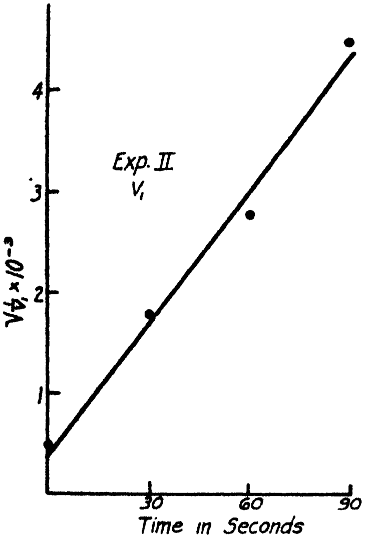


FIG. 8

The experimental data on the rate of rapid agglutination of red blood cells are therefore in fairly good agreement with the reported results with colloids and with v. Smoluchowski's theory. But when we come to the calculation of R/r i.e., the ratio of the radius of the cell to its sphere of attraction, a striking difference appears. Whereas the largest values heretofore obtained is 13.7 (Ehringhaus and Wintgen), our values range from 142.3 to 2513, the average of all experiments being 653.0. In the equation $R/r = \frac{\beta}{2/3\ H\Theta/N\eta\ V_0}$ the quantity $2/3\ H\Theta/N\eta$ is practically a constant for ordinary temperatures, so that the value of R/r depends almost wholly on the ratio β/V_0. In all of our experiments the value of V_0 is small as compared to the concentrations of colloids used by other investigators. Our values for β, on the contrary, do not, except in a few instances differ markedly from those obtained by others. This follows from the fact that the absolute rate of the agglutination of the weak cell suspension is almost as rapid as that of the coagulation of the concentrated colloidal solution.

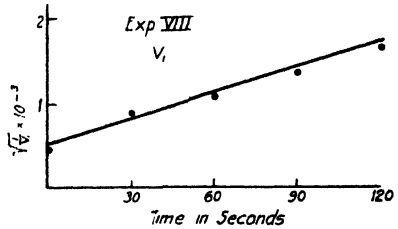


FIG. 9

In order for agglutination of the cells to proceed as rapidly as coagulation of the particles there are at least two differences in the suspensions which must be compensated for if their units are to come in contact and form aggregates at equal rates. In the first place, the red blood cells are farther apart. Comparing one of Westgren and Reitstötter's experiments with our experiment IX, their particles are 7.9×10^{-4} cm. apart whereas the red blood cells are 35.4×10^{-4} cm. apart. This gives a ratio,

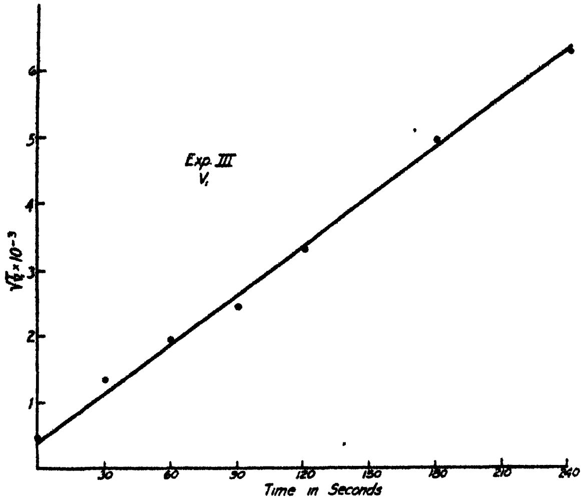


FIG. 10

$$\frac{\text{Distance between cells}}{\text{Distance between particles}} = 4.4$$

The second factor is that the Brownian movement of red blood cells is relatively slight. From the formula $\Delta^2 = RT/N \cdot 1/3\pi\eta r \cdot t$, where Δ = average distance; R = 8.31×10^7 (gas constant); N = 6.06×10^{23} (Avogadro's constant); T = absolute temperature; t = time in seconds; η = coefficient of viscosity; r = radius of particle. The Brownian movement of the gold particles in the experiment cited above which have a radius of 96$\mu\mu$ is 19.2 ×

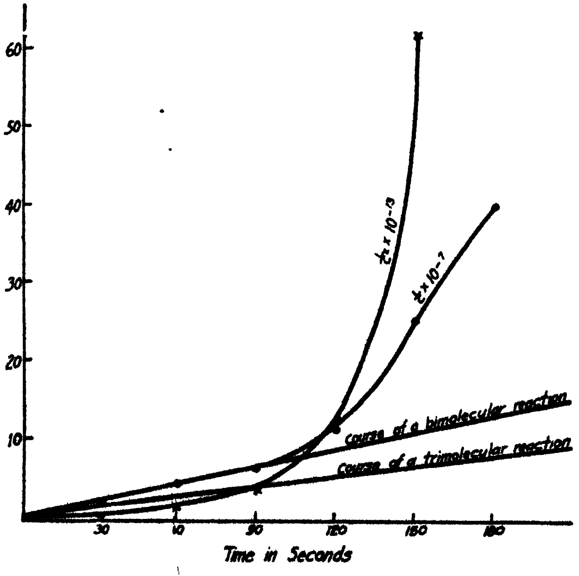


FIG. 11

10^{-5} cm. per second. The Brownian movement of the red blood cells used, which have a radius of 2600$\mu\mu$ is *theoretically* 4.05×10^{-5} cm. per cc. This gives a ratio

$$\frac{\text{Brownian movement of cells}}{\text{Brownian movement of particles}} = 0.21$$

and the ratio

$$\frac{\text{Distance ratio}}{\text{Brownian movement ratio}} = 20.95$$

In actual fact this ratio of discrepancy between the two types of suspensions is certainly much larger, as the red cells have even less Brownian movement than the theory would indicate. Practically speaking they have none when one considers the distance which separates them in our suspensions.

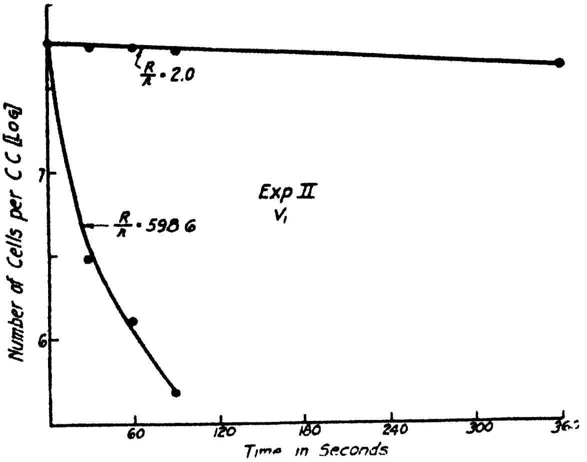


FIG. 12

It is therefore evident that some factor must operate to enable the red blood cells to form, as they do, aggregates as rapidly as colloidal particles. This unknown factor may well be included in what is considered a larger attration sphere. This necessity for a large attraction sphere is shown graphically in Fig. 12, where the upper curve illustrates what the course of agglutination in experiment II would be if $R/r = 2.0$, and the lower curve illustrates the actual data where $R/r = 598.6$. In other words the maximum range of effective attraction between the cells in this experiment was 0.15 cm!

We have at present no explanation to offer for this remarkable difference between the cell suspensions and the colloidal solutions in regard to the "radii of attraction" of their particles. The cells and particles themselves differ in at least two ways. The cells are relatively enormous, their volume being approximately 50,000 times that of the gold particles. They also bear a different relation to the surrounding medium than does the gold particle as they are permeable to water and certain ions. Mass effects and surface energies may therefore differ considerably in the two cases and these may account for the relatively large "sphere of attraction" that is observed in the rapid agglutination of the red cells. An investigation of these problems is in progress.

REACTIONS OF THE TYPE $Cl_2 + 2\ KOH = KCl + KClO + H_2O$[1]

BY F. W. BERGSTROM[2]

Introduction and Discussion

Potassium amide[3] reacts readily with strongly electropositive elements such as sodium, lithium, and calcium, more slowly with magnesium, aluminum and lanthanum, and very slowly with cerium, zinc and manganese[4]. Elements between cadmium and cobalt in the electropotential series fail to react with solutions of potassium amide. A solution of this base was found to react very slowly with lead and bismuth, more readily with tin, antimony, arsenic, and tellurium, and very readily with selenium, sulfur, and iodine. Potassium amide thus reacts most readily with strongly electropositive or strongly electronegative elements, while the rate of reaction approaches zero in the case of elements of intermediate electroaffinity, such as cadmium, iron, and cobalt.

The reactions with these classes of elements were found to differ in type. Strongly electropositive elements react initially with basic amides with the formation of solutions of the more electropositive metal:

$$(1)\ Al + 3\ NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3\ Na.^{5}$$

Subsequent reactions of sodium upon the solvent and of sodium amide on the amphoteric base, aluminum amide, lead to the formation of sodium ammono-aluminate, $Al(NH_2)_2NHNa \cdot NH_3$:

The initial reaction of an electronegative element with potassium amide is similar to that of chlorine with a cold dilute solution of potassium hydroxide in water:

$$(2)\ Cl_2 + 2\ KOH = KCl + KClO + H_2O.$$

Some other reactions of this type[6] that have been recognized in aqueous solution are the following:

---

[1] The Action of Solutions of Ammono Bases in Liquid Ammonia on Elements more Electronegative than Nickel.

[2] National Research Fellow.

[3] Potassium amide is a base in ammonia, just as potassium hydroxide is a base in water. Franklin: J. Am. Chem. Soc. **46**, 2139 (1924).

[4] Franklin: J. Am. Chem. Soc. **35**, 1463 (1913); J. Phys. Chem. **23**, 41 (1919); J. Am. Chem. Soc. **37**, 2300 (1915); Fitzgerald; **29**, 660 (1907); Bergstrom, **45**, 2788 (1923); **46**, 1548, 1552. (1924); **47**, 1836 (1925).

[5] In general terms, $M^n + nANH_2 \rightleftharpoons M(NH_2)n + nA$, where M is a metal, such as aluminum, of positive valence, n, and A is an alkali metal. See Kraus and Kurtz: J. Am. Chem. Soc., **47**, 45 (1925); Bergstrom: **45**, 2788 (1923); **47**, 1836 (1925)

[6] Mellor: "A Comprehensive Treatise on Theoretical and Inorganic Chemistry," vol. 2, p.50 (1922); Tartar and Draves: [J. Am. Chem. Soc. **46**, 574(1924)]. Arsenic, phosphorus, and silicon react with alkali hydroxides to give as one of the reaction products, respectively, arsine, phosphine, and hydrogen. Winter [J. Am. Chem. Soc., **26**, 1509 (1904)] correctly considers that sodium phosphide is one of the primary products of the action of sodium hydroxide on phosphorus. Sodium phosphide is readily converted by hydrolysis to phosphine and sodium hydroxide. Undoubtedly, sodium arsenide is one of the primary products of the reaction of sodium hydroxide upon arsenic. Arsine is, of course, readily formed by hydrolysis of sodium arsenide.

(3) $F_2 + 2\ KOH = 2\ KF + H_2O + 1/2\ O_2$

(4) Iodine and bromine react initially as in (2)

(5) $(2x + 2)S + 6\ KOH = 2\ K_2S_x + K_2S_2O_3 + 3\ H_2O.$

(6) $(2x + 1)Se + 6\ KOH = 2\ K_2Se_x + K_2SeO_3 + 3H_2O.$

(7) $(2x + 1)Te + 6\ KOH = 2\ K_2Te_x + K_2TeO_3 + 3\ H_2O.$

It is the purpose of the present investigation to examine in detail reactions of this type occurring in liquid ammonia as solvent.

It was found that elements more electronegative than nickel react with solutions of potassium amide, and, to a less extent, with solutions of other ammono bases, provided that the alkali metal salts of that element are soluble in ammonia.[1, 2] $Na + NH_3 \longrightarrow \frac{1}{2}H_2 + NaNH_2$, a reaction catalyzed by Al and $Al(NH_2)_3$; $NaNH_2 + Al(NH_2)_3 \longrightarrow Al(NH_2)NHNa{\cdot}NH_3$.

Tin reacts with sodium or potassium hydroxide to form a stannite and hydrogen, while phosphorus reacts with this base to form a hypophosphite and phosphine. In view of the fact that potassium amide reacts with these elements in ammonia initially according to the type reaction illustrated by equation (2), it is probable that the reactions of these elements and arsenic with bases in water all take place in an analogous manner. Due to hydrolysis, the alkali stannides formed by the action of sodium or potassium hydroxide on tin are converted to stannane, SnH_4, which is unstable and decomposes to give tin and hydrogen.[3]

No satisfactory mechanism has heretofore been proposed for the action of aqueous solutions of bases upon tin.[4]

The Reaction between Potassium Amide and Iodine

Iodine reacts very rapidly with potassium amide at −33° with the formation of potassium iodide and nitrogen, according to the equation (8) $6\ I + 6\ KNH_2 = 6\ KI + 4\ NH_3 + N_2$. Obviously, this reaction is analogous to the action of fluorine on a solution of potassium hydroxide.(3). Calculated from (8), 29.4 cc. of nitrogen (standard conditions) would be liberated by the action of potassium amide upon one gram of iodine. Experimentally there was collected 38.6 and 37.8 cc. nitrogen (reduced to standard conditions) when 1.160 and 1.118 g. iodine reacted with an excess of potassium amide. This corresponds respectively to 33.3 and 33.9 cc. nitrogen per gram of iodine. The apparatus used for collection of gas was not altogether satisfactory. Iodine was melted into glass tubes of 5 mm. diameter, convenient lengths of

---

[1] Potassium and sodium form soluble salts of homo-atomic anions containing lead, tin, bismuth, antimony, arsenic, phosphorus, tellurium, selenium, sulfur, iodine. Kraus; J. Am. Chem. Soc. **44**, 1220 (1922). E.g, K_4Pb_9, Na_3Sb_7, Na_2Te_4, K_2Se_5, K_2S_x, etc.

[2] The initial reactions may be expressed by the general equation

$$(1 + m/n)M + nANH_2, = m/nM(NH_2)_n + AmM$$

where m is the negative and n the positive valence of the element M. In general, one or both of the products on the right hand side of the equation react further with those on the left hand side. Kraus: Trans. Am. Electrochem. Soc. **45**, 185 (1924).

[3] Kraus: J. Am. Chem. Soc. **44**, 179 (1922). The alkali stannides are analogous to the KCl of equation (2), while the stannites are analogous to KClO.

[4] Cf. Mellor: "A Comprehensive Treatise, etc"., Vol. 2, p. 509 (1922).

this tube were cut off and introduced rapidly into a reaction vessel, cooled by a bath of liquid ammonia at −33°. Gases evolved in the reaction were passed through a mercury trap into a large tube filled with water to absorb ammonia, thence being drawn through phosphorus pentoxide tubes by a Töpler pump, and so transferred to an apparatus for gas analysis. By the action of sodium amide on iodine at very low temperatures, Ruff[1] prepared a substance of the composition Na_2NI_3, which probably consisted in part of a sodium ammonohypoiodite. Substances have been prepared[2] which may be regarded as salts of ammono hypoiodous acid, INH_2 or I_2NH.(= $NI_3 \cdot xNH_3$).

The Reaction between Basic Amides and Sulfur

Sulfur reacts very readily and without evolution of gas with a solution of potassium amide at −33° initially to form a yellow precipitate, which subsequently goes into solution because of further reaction with sulfur. Sulfur readily reacts with the amides of lithium, calcium, barium and magnesium while a solution of sulfur in liquid ammonia at 20° more slowly reacts with cobaltous and mercuric nitrides and lead imide. It appears from this work that there are obtained derivatives of ammonosulfurous acid, $S(NH)_2$, of ammonothiosulfuric acid, $S_2(NH)_2$, and perhaps of other ammono sulfur acids.[3]

The Reaction between Ammono Bases and Selenium

Selenium reacts readily with potassium amide solution at −33° or room temperature initially with the formation of a white precipitate which contains a very explosive substance, probably a potassium salt of selenium amide or imide, and potassium monoselenide. Further reaction with an excess of selenium leads to the formation of highly colored solutions containing polyselenides of potassium and a soluble, non-explosive potassium salt of a complex ammono acid containing selenium.[4] Selenium was found to react readily with the amides of sodium, lithium, and barium. Calcium amide attacks selenium at a very slow rate, probably because of the low solubility of the products of the reaction. No gas was evolved in the reaction between selenium and potassium amide at −33°, although small amounts were obtained when the reaction was carried on at room temperature.[5]

The Reaction between Potassium Amide and Tellurium

Tellurium reacts fairly readily with potassium or sodium amides at room temperature, although only very slowly at −33°. In the presence of an excess of tellurium, soluble alkali polytellurides are formed, the insoluble product of the reaction probably being an ammonotellurite or tellurate. Attempts to analyze this substance resulted in violent explosions.

---

[1] Ber. **33**, 3025 (1900).

[2] Szuhay: Ber. **26**, 1933 (1893); Silberrad: J. Chem. Soc. **87**, 68 (1905).

[3] Derivatives of ammonosulfurous and ammonothiosulfuric acids have been prepared by Ruff and Geisel: Ber., **37**, 1573 (1904). A more complete discussion of the ammono acids of sulfur will appear in a forthcoming paper.

[4] This salt may possibly bear some analogy to the thiosulfates.

[5] For method of determining this gas, see J. Am. Chem. Soc. **47**, 2320 (1925).

The Reaction between Basic Amides and Arsenic, Antimony, and Bismuth

Arsenic and antimony react slowly with a solution of potassium amide at room temperature with the production of red solutions indicative of the presence of complex anions containing these two elements.[1] Sodium amide reacts slowly with arsenic and very slowly with antimony. Potassium amide, and more particularly sodium amide, react with extreme slowness with bismuth.

The Reaction between Basic Amides and Phosphorus

Red and yellow phosphorus both react readily with potassium amide at room temperature to form a solution containing a polyphosphide of potassium and a light yellow precipitate, perhaps a potassium ammonophosphite. Sodium amide reacts in a similar manner with red phosphorus.

The Reaction between Basic Amides and Tin

Tin was found to react slowly with sodium amide and with a dilute solution of potassium amide with the formation of deep red solutions containing sodium or potassium ammonostannites and polystannides, in accordance with the equation:[2,3,4]

$$(9)\quad 10Sn + 6\ KNH_2\ (\text{or}\ NaNH_2) = 2SnNK\cdot 2NH_3\ (\text{or}\ SnNNa\cdot 2NH_3) + K_4Sn_8\ (\text{or}\ Na_4Sn_8)$$

The stannites may be alternately formulated as $Sn(NH_2)_2\cdot KNH_2$, $Sn(NH_2)_2\cdot NaNH_2$ or as $K(Sn(NH_2)_3)$, $Na(Sn(NH_2)_3)$. Tin, while dissolved at a very slow rate by lithium amide, fails to react appreciably with barium or calcium amides at room temperature.

Potassium and sodium ammonostannites are white solids, very readily soluble in liquid ammonia and are thus easily distinguished from potassium ammonostannate, which is only very slightly soluble.[5] The stannites react very vigorously with water without the formation of appreciable quantities of nitrogen or hydrogen. That potassium and sodium ammonostannites are derivatives of divalent tin was verified by preparing the potassium salt by the action of potassium amide on stannous chloride.

Although potassium amide in dilute solution at room temperature reacts slowly with tin, the reaction in the more concentrated solutions is practically negligible, owing to the formation of passive coating over the metal. (See Fig. 1) This passive coating could be removed by the action of a solution of ammonium chloride—an acid in ammonia—or even by the long continued action of the pure solvent, so was probably a very slightly soluble potassium tin alloy. Sodium amide was found to react more smoothly and readily with tin without the formation of a passive coating over the metal. The formation of this coating evidently depends upon the initial concentration of the reacting base. Sodium amide is soluble only to the extent of about a gram per liter in liquid ammonia at ordinary temperatures, while potassium amide is very soluble.

---

[1] Peck: J. Am. Chem. Soc. 40, 335 (1918).

[2] It is not certain, although it is very probable, that the ammono salt first formed is a derivative of divalent tin, for potassium ammonostannate was found to react very slowly with tin to form potassium ammonostannite. Thus, a tin rod in contact with an excess of crystals of potassium ammonostannate in liquid ammonia for three weeks at room temperatures lost 7 mg. in weight.

[3] For a discussion of intermetallic compounds of this type, see Kraus: J. Am. Chem. Soc., 44, 1216 (1922).

[4] Kraus: J. Am. Chem. Soc., 44, 179 (1922).

[5] Fitzgerald: J. Am. Chem. Soc. 29, 1692 (1907).

Experimental Work:

The equations given for the reactions between tin and the amides of sodium and potassium have been verified (1) by determination of the amount of tin dissolved by weighed quantities of potassium or sodium amides at room temperature; (2) by the approximate determination of the ratio of alkali metal in the ammono salt formed to the total quantity of alkali metal used in the reaction; (3) by analysis of the ammono salt.

The solubility of tin in potassium or sodium amide solutions was determined by allowing a known amount of the ammono base to react with a weighed tin rod, the weight of the rod again being determined after the attainment of equilibrium. Sodium and potassium amides were prepared by the action of liquid ammonia, in the presence of iron wire, which acts as a catalyst, upon weighed quantities of the corresponding alkali metal.[1] Tin was used in the form of slender rods, obtained by melting the metal in a vacuum and allowing it to flow into a glass tube of 5-6 mm. internal diameter, which served as a mold. The glass was readily removed from the tin by suddenly chilling the still hot tube in water.[2]

It was found convenient to use a three-legged glass reaction tube, the legs containing respectively alkali metal plus iron wire catalyst, the weighed rod of tin, and mercury. The alkali metal amide was transferred quantitatively to the leg containing the tin and allowed to react with this metal from two to twelve months. In order to remove the alkali metal polystannide, the deep red solution resulting from this reaction was washed into the leg containing the mercury, in which this alloy is soluble.[3] The leg of the reaction tube containing the tin was opened[4] the tin removed and weighed, and the leg cleaned and sealed up again. Into this leg was then decanted the colorless solution of the stannite, which was evaporated to dryness, the resulting solid being dried in a vacuum and submitted to analysis. The ammonia in the reaction tube was evaporated into a tared flask of water and so determined.

The solubilities of tin in sodium and potassium amide solutions, as thus determined, are plotted in Fig. 1. against the concentration. The average atomic ration of tin to alkali metal in the case of tin–sodium amide is 1.65. The maximum ratio in the case of tin–potassium amide is 1.70. These values would indicate Na_4Sn_8 or K_4Sn_8 to be formed in the reactions represented by equation (9). It is possible that some alkali ammonostannate is formed simultaneously with the stannite, for a very small amount of white matter, very slightly soluble in ammonia, is invariably present at the end of a reaction.

---

[1] Kraus and Chiu: J. Am. Chem. Soc. **44**, 2001 (1922) give directions for preparing sealed glass capsules containing weighed quantities of sodium or potassium.

[2] Compare method of Kraus and Chiu for preparing sticks of tellurium. ibid, p. 2002.

[3] Bergstrom: J. Am. Chem. Soc. **47**, 1506 (1925).

[4] The manipulations required for the preparation of substances in liquid ammonia solution will readily be understood from previous articles. Franklin and others: J. Am. Chem. Soc. **27**, 832 (1905); **29**, 1694 (1907); **35**, 1460 (1913); **46**, 1545 (1924); J. Phys. Chem. **15**, 915 (1911); **16**, 694 (1912). In these reactions, the stopcock of the reaction tube was sealed off to prevent gradual loss of ammonia.

In the reactions between sodium or potassium amides and tin amalgam, nearly the theoretical amount of alkali metal initially used (33.3%, according to equation 9) was recovered in the sodium or potassium ammonostannite. In the reactions between tin and the alkali metal amides, the percentage of the alkali metal found in the ammono salt was frequently close to 33%, and at times several percent lower, due chiefly to experimental error.

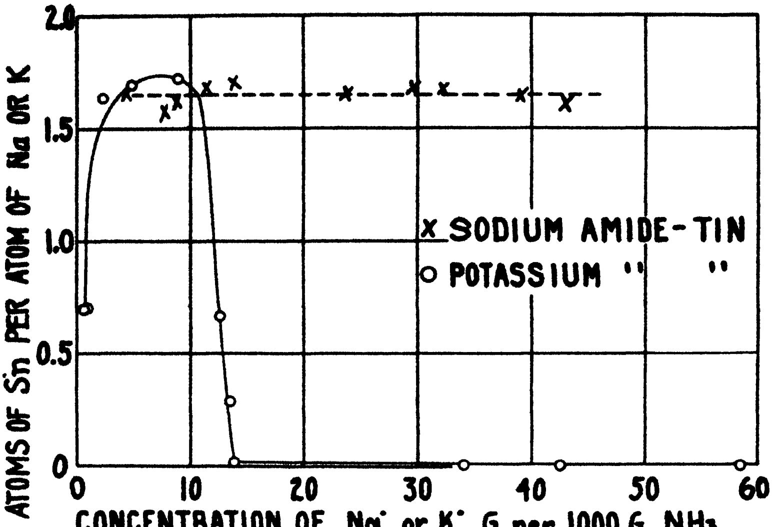


FIG. 1

Preparations of Potassium Ammonostannite.

Specimen (1) was prepared by the action of mercury on the product of reaction of tin with potassium amide, specimens (2) and (3) by the action of potassium amide upon an excess of tin amalgam, and (4) and (5) by the action of potassium amide upon stannous chloride: $3KNH_2 + SnCl_2 = 2KCl + SnNK \cdot 2NH_3$. If potassium amide is not used in excess of the quantity demanded by the equation, the only soluble product of the reaction is potassium ammonostannite. Potassium chloride is only slightly soluble in ammonia. Some reduction of the stannous chloride evidently takes place, the resulting tin reacting with potassium amide to give a light red solution containing a potassium polystannide, which decolorizes slowly in contact with the precipitate in the reaction tube.

Preparatory to analysis, the specimens were dried in a vacuum, hydrolyzed rapidly by water and dissolved in dilute hydrochloric acid. All of the nitrogen present in the preparations was thereby converted to ammonium chloride, in which form the nitrogen was readily determined by the customary acidimetric method. Tin was precipitated as sulfide and weighed as dioxide, but the method was not satisfactory, giving low results for tin. Potassium was determined as sulfate in the filtrate from the tin sulfide.

No.	Wt. subs. dried in vacuo at (°).		Wt. of SnO_2 in () of subs.		Wt. of nitrogen in () of subs.		Wt. of K_2SO_4 in () of subs.	
1	(20°)	0.1118g			(1/2)	0.01090g.	(1/2)	0.0248g.
2	(20°)	0.5454			(1/4)	0.02839	(1/2)	0.1160
3	(20°)	0.5967	(3/4)	0.3232g	(1/4)	0.02968	(3/4)	0.1855
4	(-40°)	0.4684						
	(20°)	0.4677	(1/4)	0.0838	(1/4)	0.02375	(1/2)	0.1031
5	(20°)	0.2827	(1/4)	0.0513	(1/4)	0.01459	(1/2)	0.0629

Preparations of Sodium Ammonostannite.

Specimen (1) was prepared from sodium amide and tin amalgam. The remainder of the preparations were made by the action of mercury on the product of reaction of sodium amide and tin. Sodium ammonostannite was analyzed in the same manner as the potassium salt.

No.	Wt. subs. dried in vacuo at ()°		Wt. of SnO_2 in () of subs.		Wt. of nitrogen in () of subs.		Wt. of Na_2SO_4 in () of subs.	
1	(20°)	0.5042g	(3/4)	0.2977g	(1/4)	0.01757g	(3/4)	0.1451g
2	(20°)	0.6507	(1/4)	0.1265	(1/4)	0.03617	(1/2)	0.1244
3	(20°)	0.7334	(1/4)	0.1446	(1/4)	0.04077	(1/4)	0.0701
4	(20°)	0.1979	(1/2)	0.0766			(1/2)	0.0377

Summary of Analyses

(Dried in a vacuum at 20°)

	Calc. for $SnNK \cdot 2NH_3$	1	2	3	4	5
Sn	57.7			56.9	56.5	57.2
N	20.4	19.5	20.8	19.9	20.3	20.6
K	19.0	19.9	19.1	18.6	19.8	20.0
	Calc. for $SnNNa \cdot NH_3$					
Sn	62.6	62.0	61.3	62.2	61.8	
N	22.1	22.1	22.2	22.3		
Na	12.1	12.4	12.4	12.2	12.3	

The analyses are satisfactory, considering the fact that the salts were too soluble in ammonia to be purified by crystallization from this solvent.

The Reaction between Solutions of the Basic Amides and Lead.

Lead was found to behave in a very erratic manner. At times this metal reacted very slowly with a solution of potassium amide with the formation of a green solution containing potassium polyplumbide, and, presumably, potassium ammonoplumbite; while, at other times, apparently under the identical experimental conditions reaction failed to take place. This is probably due to the condition of the surface of the lead. Sodium amide, in two experiments, failed to react with lead over a period of several months.

The Reactions between Solutions of Potassium Amide and Others of the more Electronegative Elements and Their Amalgams.

A 0.6 normal solution of potassium amide failed appreciably to attack gold in four months, or copper in nine months at room temperature. Germanium, either in powder or lump form was not appreciably attacked in two months. Mercury, which had been distilled in a vacuum, but not in a current of air[1] was attacked at an extremely slow rate. Lead, bismuth, silver amalgams were not appreciably attacked by a solution of potassium amide, while the amalgams of copper and gold were attacked very slowly, and tin amalgam was attacked much more rapidly.

In conclusion, the author wishes to express his thanks to Dr. C. A. Kraus for his kind and helpful interest in this work.

Summary

(1) Potassium amide reacts with lead and all elements more electronegative than lead, provided the alkali metal salts containing these elements in homo-atomic anions are soluble in liquid ammonia. These reactions are all of the type of the reaction between chlorine and a cold dilute solution of potassium hydroxide: $Cl_2 + 2KOH = KClO + KCl + H_2O$. Thus, the equation for the reaction of potassium amide with an excess of tin is $10Sn + + 6KNH_2 = K_4Sn_8 + 2SnNK\cdot 2NH_3$.

(2) The reactions between aqueous solutions of bases and tin, arsenic or phosphorus are likewise of the type $Cl_2 + 2KOH = KClO+KCl+H_2O$ The hydrogen obtained in the first instance, and the arsine and phosphine in the second and third undoubtedly result from secondary reactions of water on potassium stannide potassium arsenide, and potassium phosphide.

(3) Potassium and sodium ammonostannites have been prepared. The constitution of these salts may be represented by the alternate formulas:

$$Sn(NH_2)_2\cdot KNH_2,\ SnNK\cdot 2NH_3 \text{ or } K[Sn(NH_2)_3];$$
$$Sn(NH_2)_2\cdot NaNH_2,\ SnNNa\cdot 2NH_3, \text{ or } Na[Sn(NH_2)_3].$$

---

[1] Hulett: Phys Rev. 33, 397 (1911) states that mercury prepared in this manner is not quite pure.

THE ANTAGONISTIC ACTION OF IONS IN THE NEUTRALIZATION OF SOLS

BY HARRY B. WEISER

In the precipitation by electrolytes of sols stabilized by preferential adsorption of ions, it is usually considered that only anions count in the case of positive sols and only cations count in the case of negative sols. However, it was recognized by Freundlich[1] a score of years ago that the critical precipitation concentration of electrolytes for sols may be influenced by the ion having the same charge as the sol; and a decade ago Bancroft[2] pointed out that the amount of electrolyte required to precipitate any given suspension will vary with the nature of the cation, the anion and the disperse phase. This point of view does not seem to have been taken seriously by many people; but in 1920, attention was called[3] to the fact that the influence of the ions having the same charge as the sol cannot be disregarded entirely in any case, and may be quite marked if the electrolyte precipitates only in high concentration. The precipitation value of electrolytes for sols was therefore defined as that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the precipitating solution. There is thus an antagonistic action between the oppositely charged ions of a precipitating electrolyte in the sense that the greater the adsorption of the stabilizing ion the greater must be the adsorption of the precipitating ion to effect neutralization. Hence the precipitation value of an electrolyte with a strongly adsorbed stabilizing ion is necessarily higher than that of an electrolyte with a weakly adsorbed stabilizing ion.

Recognition of the importance of the stabilizing ion in the precipitation of sols by electrolytes lead directly to a plausible explanation of the manner in which the precipitation value varies with the concentration of sol and furnished a partial explanation of the behavior of certain mixtures of electrolytes with certain sols. Within the past year there has appeared a number of papers by Dhar, Sen and Ghosh[4] more than 150 pages to date, which further emphasize the action of ions having the same charge as the sol. Since the relation of this work to the work of the author is not always clear, particularly in the later papers, it seems advisable to consider the phenomena studied earlier by the author in the light of the observations of Dhar and his collaborators, Of these phenomena, the influence of dilution of sols on their stability toward electrolytes and the "acclimatization" of sols will be discussed briefly;

---

[1] "Kapillarchemie", 352 (1909); Z. physik, Chem., **44**, 104 (1903).

[2] J. Phys. Chem., **19**, 363 (1915).

[3] Weiser: J. Phys. Chem., **24**, 30 (1920).

[4] J. Phys. Chem., **28**, 313, 457, 1029 (1924); **29**, 435, 517, 659 (1925); Kolloid-Z., **34**, 262 (1924); **36**, 129 (1925); Z. anorg. Chem., **142**, 345 (1925). See also Mukherjee and Ghosh: Quart. J. Indian. Chem. Soc., **1**, 213 (1924).

while the action of mixtures of electrolytes on sols will receive detailed consideration.

Effect of Dilution of Sols on their Stability toward Electrolytes

From an investigation of the influence of the concentration of sols on their precipitation by electrolytes the following conclusions were formulated:[1]

(1) The manner in which the precipitation value of an electrolyte varies with the concentration of colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilizing ion.

(2) If the adsorption of the stabilizing ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large, the precipitation value varies almost directly with the concentration of the colloid. This condition may be realized experimentally with electrolytes having trivalent and tetravalent precipitating ions which precipitate in extremely low concentration.

(3) If the adsorption of the stabilizing ion of an electrolyte is appreciable, the precipitation value is increased. This effect is more pronounced the greater the dilution of the colloid, since the decreased opportunity both of collision and coalescence of particles combines to render the colloid proportionately more stable so that proportionately more of the precipitating ion must be added for complete coagulation. The influence of adsorption of the stabilizing ion is more marked with electrolytes having univalent precipitating ions which precipitate only in very high concentration. Under these conditions, the precipitation value falls off much less sharply than under the conditions given in (1) and may even increase as the concentration of the colloid is decreased.

A survey of the work of the Allahabad laboratory dealing with this subject, discloses merely an extension of the number of cases studied, without contributing anything to the general principles formulated above. The confirmatory data are, of course, valuable; but it is too bad that an attempt at classifying the data leads to the enunciation of a "general dilution rule, that the greater the concentration of a sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valence of the precipitating ion." This qualitative statement holds whenever the adsorption of the stabilizing ion is small relatively to that of the precipitating ion; but there are necessarily many exceptions to it. Some of these are mentioned; but it is obvious that the list could be extended greatly if there were any point in doing so. Since the precipitation value of an electrolyte depends on the nature of the anion, and of the cation and on the nature of the sol, one might expect the same sol to behave differently with different electrolytes having the same precipitating ion and a different stabilizing ion. Indeed Ghosh and Dhar[2] found that the "rule" was followed with positive ferric oxide sol using potassium chloride[3] but was "abnormal" if aluminum nitrate was the precipitating electrolyte;

---

[1] Weiser and Nicholas: J. Phys. Chem., **25**, 742 (1921).

[2] J. Phys. Chem., **29**, 659 (1925).

[3] Note: The results with potassium nitrate are similar to those with potassium chloride.

a result that might be expected from (3) above. Such a rule as Dhar has set down seems to me to be a positive menace rather than a help, if its limitations and the principles on which it is based are not recognized clearly; and if these are recognized, the qualitative rule is superfluous, particularly when one can find exceptions whenever one looks for them.

It was somewhat disconcerting to find Dhar and his collaborators accepting in principle, the author's explanation of the influence of dilution of sols on their stability toward electrolytes, when the former were laboring under the mistaken idea that the most readily adsorbed ion precipitates in highest concentration, the converse of which is that the least adsorbed ion having the same charge as the sols is the strongest stabilizing ion. It is gratifying, however, to find Ghosh and Dhar[1] at last attributing the higher precipitation values for arsenious sulfide sol of potassium sulfate, potassium citrate and potassium ferrocyanide as compared with potassium chloride, to stronger adsorption of the multivalent ions than of univalent chloride. Other advocates of Freundlich's adsorption theory of the stabilization and precipitation of sols had reached this conclusion many years ago.

The Acclimatization Phenomenon

The amount of electrolyte which will cause complete precipitation when added rapidly, frequently will not do so when it is added dropwise through a long interval of time. In attempting to arrive at the cause of this phenomenon of "acclimatization"[2], it was noted that the slow addition was always accompanied by fractional precipitation of the sol, and I attributed the excess required on slow addition to the continuous removal of ions owing to adsorption by neutralized particles. On this basis the factors which determine the excess of electrolyte required for a given slow rate of addition are: (1) the extent to which the colloid undergoes fractional precipitation; (2) the adsorbing power of the precipitated colloid; and (3) the adsorbability of the precipitating ion. At the time this communication was written I had not studied the effect of dilution of sols on their stability toward electrolytes and so did not know enough to call attention to the fact that the effect is greatest when the precipitation value of the electrolyte increases with decreasing concentrations of sol, such as obtains in the precipitation of arsenious sulfide sol with potassium chloride. In this case, the fractional precipitation accompanying the dropwise addition of potassium salt produces sols that are successively more and more stable, so that a relatively larger amount of electrolyte is necessary for complete precipitation. Recognizing this fact, it was only necessary to modify the third factor in my original paper to read: (3) the relative adsorbability of the precipitating and stabilizing ions. This modification was made in a chapter on adsorption written two years ago for a book being compiled by J. Alexander.

---

[1] Kolloid-Z., **36**, 129 (1925).

[2] Weiser: J. Phys. Chem., **25**, 399 (1921).

Dhar, Sen and Ghosh have repeated and extended the experiments on the acclimatization phenomenon and attribute it to adsorption of the stabilizing ion without entering into the mechanism of the action. Had they done so, they would have recognized that strong adsorption of the stabilizing ion is not essential in case there is strong adsorption of the precipitating ions during fractional agglomeration. On the other hand, strong adsorption of the stabilizing ion is important, if not essential, in case the successive dilutions of the sol by fractional precipitation is the determining factor. In either case, acclimatization to a greater or lesser degree is a necessary concomitant of fractional precipitation.

It should be pointed out, in passing, that acclimatization of hydrous ferric oxide precipitated by aluminum nitrate would be expected in view of the increasing precipitation value of this electrolyte with decreasing concentration of sol; however, one should not overlook the stabilizing effect of colloidal hydrous aluminum oxide formed by hydrolysis of the diluted electrolyte. I should not be surprised if this were the more important factor in increasing the precipitation value on slow addition of the electrolyte.

The Precipitation of Sols by Mixtures

From a study of the precipitation of sols by mixtures of electrolytes, the following conclusions were drawn in 1921:[1]

(1) The precipitating action of mixtures of pairs of electrolytes is approximately additive if the precipitating power of each is of the same order of magnitude; but may be far from additive if the electrolytes have widely varying precipitating power. In the latter case the action of the electrolytes is "antagonistic", in the sense that relatively more of each is necessary than if the other were absent.

(2) In the simultaneous adsoption by solids from mixtures of two electrolytes having no ion in common, the most strongly adsorbed cation and anion are taken up most and the other pair least readily; from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the others were absent but the most readily adsorbed ion is displaced the least.

(3) Factors which influence the precipitating action of mixtures of electrolytes are (1) the effect of the presence of each precipitating ion on the adsorption of the other and (2) the stabilizing action of the ions having the same charge as the colloid. The second factor is of minor importance with mixtures of electrolytes that have similar precipitation values and have stabilizing ions in common.

In discussing the action of potassium chloride on colloidal arsenious sulfide it was noted "that the sol probably owes its stability to preferential adsorption of HS′ ion derived from the primary dissociation of hydrogen sulfide. If enough potassium chloride is added to this colloid, the adsorption of potassium ion will neutralize the combined adsorption of the stabilizing ions, HS′ and Cl′. In this particular case the high precipitation value of potassium chloride may be due to the adsorption of Cl′ being comparable at certain concentrations to the adsorption of potassium ion. Indeed it is possible, but not proven, that at certain concentrations of potassium chloride considerable below the precipitation value, the adsorption isotherm for Cl′ may coincide with or even fall below that of potassium ion. Within this region the addition of a small amount of the strongly adsorbed barium or strontium ions may so decrease the adsorption of potassium ion that the isotherm for the latter will fall appreciably below that for Cl′." Almost exactly the same reasoning has been used by Ghosh and Dhar[1]. I represented diagramatically the relative position of the adsorption isotherms for potassium ion and chloride ion which would account for the experimental results; but pointed out that the diagram must be looked upon merely as representing a possibility that has not been verified experimentally so far. Indeed when I returned to this problem, three years later[2], I concluded from a study of adsorption during the precipitation of sols by mixtures, that the first factor mentioned under (3) above was the more important in raising the precipitation values of certain mixtures above the additive value. Thus the greater precipitation value of barium chloride in the presence of lithium chloride or potassium chloride was thought to be due chiefly to the cutting down of the adsorption of each precipitating ion by the presence of the other. Ghosh and Dhar in the first papers dealing with this phenomenon give both factors mentioned in my original paper about equal prominence but in their latest paper,[3] the influence of the stabilizing ion is looked upon as the only factor of importance, largely because the sols which show "abnormal" behavior on dilution and the phenomenon of acclimatization are "abnormal" toward mixtures of electrolytes; and since the first and second phenomena are attributed to adsorption of the stabilizing ion, the third must be. By plotting the logarithms of the concentration of one of the electrolytes added to a negative sol against the logarithms of the difference between observed and calculated values, "more or less straight lines" were obtained. This was cited as conclusive evidence of stabilization by anion adsorption; but, unfortunately, such a qualitative result would be expected if the behavior with mixtures were attributed to cationic antagonism between ions of varying adsorbability.

---

[1] Weiser: J. Phys. Chem., 25, 665 (1921).

Sen[4] arrives at the same conclusion as Dhar and Ghosh; and his experimental evidence is distinctly convincing for the case investigated. Thus, with copper ferrocyanide sol, he found an increase in precipitation value of potassium chloride and of barium chloride in the presence of potassium ferrocyanide. With mixtures of potassium chloride and potassium ferrocyanide, it is quite obvious that cationic antagonism can not come in since both precipitating cations are the same. For the first time, this raises the question whether the antagonistic action between ions of the same charge ever plays an important role in raising the precipitation value of mixtures above the additive value.

---

[1] J. Phys. Chem., 29, 453 (1925).

[2] Weiser: J. Phys. Chem., 28, 232 (1924).

[3] J. Phys. Chem., 29, 659 (1925).

[4] Z. anorg. Chem., 142, 345 (1925); J. Phys. Chem., 29, 517 (1925).

Consider the case of Graham's ferric oxide sol which owes its stability to preferential adsorption of hydrogen ion derived from hydrolysis of ferric chloride. It is too well known to need comment, that the stability of the sol falls off as the hydrogen ion concentration is decreased by dialysis and if the dialysis is continued long enough, all of the sol will precipitate. Conversely, if we add hydrochloric acid to a highly purified sol, the stability toward all electrolytes will increase. Similar stabilization would be expected on adding ferric chloride, aluminum chloride or lanthanum nitrate, as Freundlich and Wosnessensky[1] have shown. With the relatively insoluble Péan de St. Gilles sol, a maximum in the stability is reached on adding hydrochloric acid; and at a suitable concentration, the adsorption of the precipitating chloride ion neutralizes the adsorption of hydrogen ion and precipitation takes place[2] Similarly, colloidal copper ferrocyanide and Prussian blue are stabilized by preferential adsorption of ferrocyanide ion. The lower the concentration of the ferrocyanide ion the less the stability. On adding potassium ferrocyanide to a highly purified ferrocyanide sol, the stability toward all electrolytes should be increased until the concentration is high enough for the adsorption of the precipitating potassium ion to decrease the stability of the sol below the critical value. This is exactly what Sen observed with two electrolytes of widely varying precipitating power as shown by the data given in Table I and shown graphically in Figure 1. The precipitation value of both potassium chloride and barium chloride is increased to a maximum that lies above the value for either electrolyte alone.

TABLE I

Precipitation of Colloidal Prussian Blue by Mixtures. (Sen.)
(Precipitation values in millieq. per liter.)

$K_4Fe(CN)_6$	+	$BaCl_2$	$K_4Fe(CN)_6$	+	KCl
0.0		0.38	0.0		40.0
15.0		0.44	5.0		51.0
25.0		0.50	25.0		50.0
40.0		0.56	50.0		43.8
100.0		0.60	75.0		35.0
110.0		0.54	100.0		23.8
140.0		0.00	140.0		0.0

Turning to arsenious sulfide sol, we are confronted with the problem of determining whether the addition of potassium chloride, say, stabilizes the sol in the same way as potassium ferrocyanide stabilizes ferrocyanide sols. This, it will be remembered, was suggested in my original paper; but some experiments of Linder and Picton[1] are not in accord with this assumption. The latter prepared an arsenious sulfide sol with particles sufficiently fine to pass through a clay plate. On adding a few drops of a dilute solution of sodium chloride, the stability appeared unchanged but the smaller particles agglomerated so that they no longer passed through the filter. This definite evidence of agglomeration is indicative of decreased stability since, in general, stability falls off with increasing size of particles. Moreover, it is not easy to see how preferential adsorption of chloride ion would bring about agglomeration of the particles. Accordingly, the experiments recorded in the next section were undertaken.

---

[1] Kolloid-Z., **33**, 222 (1923).

[2] Weiser: J. Phys. Chem., **25**, 665 (1921).

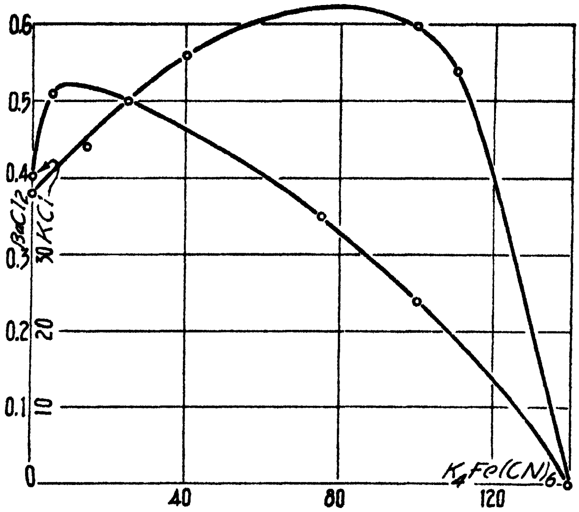


FIG. 1

Experimental

In a recent communication[2] it was shown that the same concentration of different alkali chlorides cuts down the adsorption of barium ion to widely different degrees. At the same time, barium ion doubtless cuts down the adsorption of the alkali cations to different degrees. It seemed probable, therefore, that the precipitation value of barium chloride would vary in the presence of approximately the same concentration of chloride ion but with different alkali cations. That such is the case is shown clearly by observations recorded in Table II and shown graphically in Figure 2. The precipitation values were determined exactly as described in earlier papers, by mixing 10 cc. of sol containing 0.1 g. arsenious sulfide with a definite amount of standard electrolyte diluted to 10 cc. The time of standing was 2 hours, the mixtures being shaken every one-half hour.[3] All the observations were made within two

---

[1] J. Chem. Soc., **67**, 73 (1895).

[2] Weiser: J. Phys. Chem., **29**, 955 (1925).

[3] Cf. Freundlich and Baser: Z. physik. Chem., **115**, 203 (1925).

TABLE II

Precipitation of As_2S_3 by Mixtures of $BaCl_2$ and Alkali Chlorides
(Precipitation values in millieq. per liter)

LiCl +	$BaCl_2$	NaCl +	$BaCl_2$	KCl +	$BaCl_2$	HCl +	$BaCl_2$
0.0	1.60	0.0	1.60	0.0	1.60	0.0	1.60
12.5	2.02	12.5	1.93	12.0	1.88	12.5	1.98
25.0	2.18	25.0	1.98	25.0	1.92	25.0	1.93
43.7	2.13	43.7	1.82	43.7	1.62	37.5	1.65
62.5	1.78	62.5	1.30	62.5	1.05	50.0	1.00
81.2	1.23	95.0	0.00	83.0	0.00	61.5	0.00
111.2	0.00						

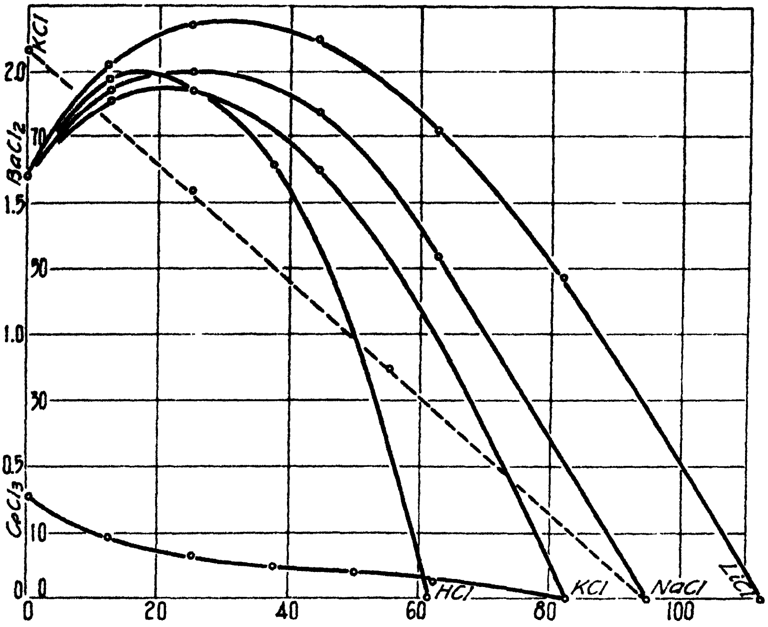


FIG. 2

days after the preparation of the sol. It will be noted that the precipitation value of barium chloride is increased by like amounts of alkali chlorides in the order LiCl > NaCl > KCl; while in the presence of HCl, the precipitation value of barium salt first rises to a point just below that in the presence of a like amount of lithium chloride and then drops off rather sharply. Since the adsorbability of the alkalis is in the order K > Na > Li,[1] it may be reasoned that the stabilizing action of chloride ion will be greater in the presence of lithium ion than of potassium ion thus accounting for the higher precipitation values of barium chloride in the presence of lithium chloride than of potassium chloride. This would not account for the behavior of mixtures of hydrochloric acid and barium chloride for, at certain concentrations of chloride, the precipitation value in the presence of the relatively strongly adsorbed hydrogen ion is similar to that in the presence of lithium ion and greater than that in the presence of either sodium or potassium ion.

---

[1] Weiser: J. Phys. Chem., **29**, (1925).

Another explanation suggests itself: For a given alkali chloride concentration, precipitation will take place when the combined adsorption of the two cations neutralizes the combined adsorption of chloride and hydrosulfide ions. The combined adsorption will be equivalent for different pairs of cations; but the relative amounts of each that make up this equivalent adsorption will vary, depending as it does on the relative adsorbability of the two cations. If one may disregard for the moment the slight variation in the amounts of chloride added with barium chloride as compared with the relatively large amount of this ion added with the alkali chloride, it follows that, for a given concentration of different alkali chlorides, the varying amounts of barium that must be added will depend on the effect of each cation on the adsorption of the other. Thus the adsorption of barium is cut down by lithium ion less than by potassium ion, tending to make the precipitation concentration of barium chloride less in the presence of lithium chloride than of potassium chloride. Hand in hand with this is the decrease in the adsorption of alkali by barium, which will tend to make the precipitation concentration of barium chloride higher in the presence of lithium. From this point of view the latter factor appears to predominate with the alkali chlorides. With hydrochloric acid however, the cutting down of the adsorption of barium by hydrogen ion is the determining factor with lower concentration of hydrochloric acid while with higher concentrations of acid the second factor appears to predominate.

To give some further indication of the influence of the stabilizing ion on the behavior of mixtures of electrolytes, some experiments were carried out on the precipitation of arsenious sulfide sol with mixtures of barium ferrocyanide with potassium ferrocyanide. The results are given in Table III and shown graphically in Figure 3. Comparing these results with those for chlorides given in Figure 2 it will be seen that the variation from additive relationships is greater with ferrocyanide than with chlorides. This is unquestionably

TABLE III

Precipitation of As_2S_3 by Mixtures of $Ba_2Fe(CN)_6$ and Alkali Ferrocyanides (Precipitation values in millieq. per liter.)

$Na_4Fe(CN)_6$	+ $Ba_2Fe(CN)_6$	$K_4Fe(CN)_6$	+ $Ba_2Fe(CN)_6$
0.0	2.25	0.0	2.25
25.0	7.10	25.0	5.75
50.0	7.75	50.0	6.20
75.0	7.50	75.0	5.60
125.0	5.25	100.0	4.40
187.0	0.00	155.0	0.00

due to the difference in the adsorbability of the stabilizing ions; but how this difference brings about the observed results is not altogether obvious. Of course, one may say that a given amount of potassium ferrocyanide stabilizes the sol more than the same amount of potassium chloride, hence the amount of barium salt necessary to precipitate the sol in the presence of potassium ferrocyanide will be greater than in the presence of potassium chloride. But there is another factor which must not be overlooked: One should expect the adsorption of both barium ion and potassium ion to be greater in the presence of ferrocyanide than of chloride on account of the stronger adsorption of the multivalent ion. It then becomes a question of fact, whether the cationic antagonism will be greater in ferrocyanide solution than in chloride solution. To determine this, 100 cc. portions of sol containing 0.95 g. arsenious sulfide were precipitated in a mixing apparatus with definite amounts of electrolyte as shown in Table IV and the adsorption determined by analysis of the supernatant solution exactly as described in earlier communications. Particular precautions were taken to secure accurate results. To avoid errors arising from adsorption of ferrocyanide, the precipitates in each instance were dissolved in concentrated sulfuric acid and reprecipitated in the usual way by pouring into water. Just as was expected, under similar conditions the adsorption of barium from ferrocyanide solution is 28 per cent higher than from chloride solution. Moreover the presence of a given amount of potassium chloride cuts down the adsorption of barium from the chloride solution 65 per cent while the same amount of potassium ferrocyanide cuts down the adsorption 75 per cent from ferrocyanide solution. This evidence of a greater

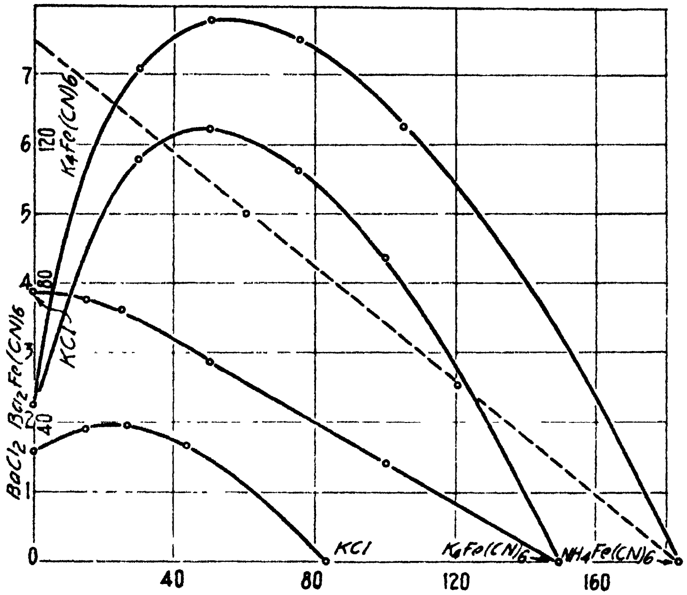


FIG. 3

TABLE IV

Adsorption of Barium Ion during the Precipitation of As_2S_3 Sol.

Solutions mixed with 100 cc. of sol. Total volume 200 cc.		BaSO$_4$ remaining in 150 cc.			Barium adsorbed millieq. per g.
		1	2	3	
N/50 BaCl$_2$	N KCl				
70	0.0	0.1146	0.1148		0.065
70	20.0	0.1199	0.1197	0.1198	0.023
N/50 $Ba_2Fe(CN)_6$	N $K_4Fe(CN)_6$				
70	0.0	0.1128	0.1126		0.082
70	20.0	0.1202	0.1198	0.1202	0.020

cationic antagonism in the presence of the more strongly adsorbed ferrocyanide ion must be considered in any interpretation of the difference in behavior of mixtures of chlorides and ferrocyanides.

Another method of attack is to determine whether the presence of relatively small amounts of potassium chloride, say, increases the precipitation value for arsenious sulfide sol of chlorides other than barium chloride. Observations with mixtures of potassium chloride with sodium chloride and cerium chloride respectively are given in Table V and plotted in Figure 2.

TABLE V

Precipitation of As_2S_3 Sol by Mixtures

KCl	+	NaCl	KCl	+	CeCl$_3$
0.0		91.0	0.0		0.388
25.0		64.0	12.5		0.230
50.0		25.0	25.0		0.162
83.0		0.0	37.5		0.132
			50.0		0.105
			62.5		0.067
			83.0		0.000

The results are quite conclusive that the addition of potassium chloride does not increase the stability of arsenious sulfide sol toward all other chlorides. Thus the relationship is approximately additive with sodium chloride whereas the precipitation value of cerium chloride is decreased unmistakably by the presence of potassium chloride. It hardly seems probable that the latter result would obtain if potassium chloride in small concentration actually stabilized the sol in the same way that a highly purified ferric oxide sol is stabilized by the addition of a small amount of hydrogen ion or ferrocyanide sols by a small amount of ferrocyanide. I have previously pointed out that in the absence of marked ionic antagonism between ions of the same sign, one might expect the precipitation values of mixtures to fall below the additive value on account of the relatively greater adsorbability of the precipitating ions at low concentrations. This was actually observed in a number of instances with hydrous oxide sols.[1] To account for the difference in the results with barium chloride and cerium chloride one should expect to find the adsorption of barium cut down much more strongly than cerium by the presence of proportionate amounts of potassium chloride. That such is the case is shown by the results recorded in Table VI on the adsorption of barium and of cerium, respectively, in the presence of 50 times the concentration of potassium chloride. Cerium was determined by the colorimetric method of Benz previously used sucessfully by Freundlich[2] in measuring the adsorption of this element by arsenious sulfide. The method was found to be entirely satisfactory when all the usual precautions in quantitive colorimetric analysis are observed. It will be noted that, under similar conditions, the adsorption of cerium is cut down less than 25 percent, while the adsorption of barium is cut down almost 85 percent.

TABLE VI

Solutions mixed with 100 cc. sol. Total volume 200 cc.		N/200 $CeCl_3$ remaining cc.		Ce adsorbed millieq. per g.
N/200 $CeCl_3$	N/2 KCl			
20	0	5.4		0.073
20	5	9.0		0.058
N/50 $BaCl_2$	N/2 KCl	$BaSO_4$ remaining in 180 cc.		Ba adsorbed millieq. per g.
30	0	0.0537	0.0537	0.064
30	30	0.0614	0.0615	0.010

In accord with my earlier conclusions, the presence of potassium chloride does not raise the precipitation concentration of sodium chloride above the additive value as would be expected if the sol was stabilized by preferential adsorption of chloride ion. The precipitation values of such mixtures having a common anion, are additive since the adsorption of the precipitating cations are similar and so the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. On the other hand, with mixtures having precipitating cations in common and different anions, one should expect variations from additive values in proportion to the difference in adsorbability of the anions. Thus, the precipitation concentrations for mixtures of potassium and sodium ferrocyanide are additive whereas the critical concentrations for mixtures of potassium chloride and ferrocyanide rise slightly above the additive values[3], because of the greater adsorbability of ferrocyanide ion than of chloride ion. (See Table VII and Figure 3.) It is of interest to note, however, that the precipitation values of potassium chloride are raised but little above the additive values by the presence of potassium ferrocyanide; and are never greater than the value for potassium chloride alone, as was observed with ferrocyanide sol. Evidently, the

---

[1] Weiser: J. Phys. Chem., **28**, 232 (1924).

[2] Z. physik. Chem., **37**, 407 (1910).

[3] Sen: J. Phys. Chem., **29**, 517 (1925).

TABLE VII

Precipitation of As_2S_3 Sol by Mixtures

(Precipitation values in millieq. per liter)

$K_4Fe(CN)_6$ +	$Na_4Fe(CN)_6$	$K_4Fe(CN)_6$ +	KCl
0	187	0.0	77.5
50	120	12.5	75.0
100	60	25.0	71.0
150	0	50.0	57.0
		100.0	28.0
		150.0	0.0

stabilizing action of ferrocyanide ion on arsenious sulfide sol is much less than on ferrocyanide sols. Since the stabilizing action of chloride on arsenious sulfide sol is much less even than ferrocyanide, it seems very doubtful whether the addition of a small amount of alkali chloride increases the stability of the sol owing to stronger adsorption of anion than of cation. As I have mentioned before, this latter view is incompatible with the filtration experiments of Linder and Picton and my precipitation experiments with mixtures of the chlorides of potassium and cerium. On the other hand, one cannot disregard the influence of the stabilizing ion as evidenced by the greater variation from additive values with mixtures of the ferrocyanides than of the chlorides of barium and potassium. We thus arrive once more at my original conclusion, formulated four years ago, that two factors may influence the precipitating action of mixtures of electrolytes: The effect of the presence of each precipitating ion on the adsorption of the other; and the stabilizing action of the ions having the same charge of the sol. The antagonistic action between precipitating ions of the same charge may influence precipitation of salt pairs only in case they show a marked difference in adsorbability. Under certain conditions, the critical values for mixtures of two electrolytes may rise above the additive values even when the precipitating ions of the two are identical, thus eliminating antagonism between precipitating ions of the same charge (Sen). For such a result there must be an appreciable difference between the adsorbability of the stabilizing ions, the magnitude of the variations from an additive relationship being determined by this difference in adsorbability.

Summary and Conclusions

1. The precipitation values for sols of mixtures of two electrolytes may be additive, may be greater than the additive values or may be less than the additive values.

2. The factors which determine the precipitation concentration of mixtures are: (1) The effect of each precipitating ion on the adsorption of the other. (2) The stabilizing action of ions having the same charge as the sol. (3) The relatively greater adsorbability of ions at lower concentrations.

3. The antagonistic action between precipitating ions of the same charge is important in raising the critical concentrations above the additive value,

only in case the ions show a marked difference in adsorbability. This effect comes in when arsenious sulfide sol is precipitated by mixtures of salts of barium and potassium.

4. Although the stabilizing action of ions having the same charge as the sol can not be eliminated, the critical values for mixtures of two electrolytes may rise above the additive value even when the precipitating ions of the two are identical, thus eliminating antagonism between precipitating ions. (Sen).

5. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion, results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by this difference in adsorbability.

6. If the first and second factors referred to in (2) are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentrations. An example of this phenomenon is the precipitation of arsenious sulfide sol by mixtures of the chlorides of potassium and cerium.

7. The influence of dilution of sol on the precipitation values of an electrolyte is determined by the nature of the anion, the nature of the cation and the nature of the sol. The "general dilution rule" enunicated by Ghosh and Dhar fails to take all of these factors into account and so is necessarily limited in its applicability.

8. Strong adsorption of the stabilizing ions of the precipitating electrolytes is not essential for the "acclimatization" of sols in case there is strong adsorption of the precipitating ions during fractional agglomeration; on the other hand, strong adsorption of the stabilizing ion is essential in case the successive dilutions of the sol by fractional precipitation is the determining factor. In either case acclimatization to a greater or lesser degree is a necessary concomitant of fractional precipitation.

Department of Chemistry,
The Rice Institute,
Houston, Texas.

PHOTOSENSITIZATION BY OPTICALLY EXCITED MERCURY ATOMS, THE HYDROGEN OXYGEN REACTION

BY ABRAHAM LINCOLN MARSHALL

Kinetic studies of gas reactions have played a very important role in the development of theories concerning the mechanism of chemical reactions. There are, however, very few such reactions occurring in the gas phase free from disturbances due to the walls of the containing vessel. Bodenstein and his co-workers have made many comprehensive studies regarding the behavior of thermal gas reactions and have accumulated a large amount of valuable data. In all of this work remarkably few truly homogeneous reactions have been found, by far the greater number taking place at some solid surface. Hinshelwood and Hughes[1] have shown that the data on the thermal decomposition of nitrous oxide, hydrogen iodide and chlorine monoxide can be completely interpreted in terms of simple thermal activation by collision, with every collision between two molecules of joint energy exceeding an amount Q leading to reaction. The thermal decomposition of nitrogen pentoxide studied by Daniels and Johnston[2] has been shown to be a unimolecular homogeneous gas reaction[3].

The studies on heterogeneous gas reactions have thrown a great deal of light[4] on the influence of the physical condition and chemical nature of the surface on the course of the reaction but have yielded practically no information on the mechanism by which the reaction proceeds at the surface.

Photochemical studies of gas reactions have given us considerable additional information on reaction mechanism in the gas phase. The number of such reactions available for exact quantitative study has in the past been limited, however, by the small absorption coefficient of many of the reactants in the wave length range available. Other complications have been secondary reactions induced in the primary products due primarily to the lack of intense sources of monochromatic radiation.

The Einstein Law of Photochemical Equivalence between quanta absorbed and molecules reacting has been of the greatest value in correlating the results of experiment. In a number of cases approximate equivalence has been found[5] and in quite a few others wide divergence. But in all these cases it has served as a starting point in studying the mechanism of these reactions. The hydrogen chlorine combination is one of the cases of wide divergence; in this case a million molecules react per quantum absorbed. It has, however, been possible to evolve a quite satisfactory mechanism for this reaction. Recently Bodenstein and Lütkemeyer[1] have studied the photochemical reaction between hydrogen and bromine and confirmed the mechanism[2] previously postulated to account for the thermal reaction[3]. They have also obtained valuable data on the rate of combination of bromine atoms: all this from an interpretation based on the Photochemical Equivalence Law.

---

[1] J. Chem. Soc. 125, 1841 (1924);
See however H. A. Taylor; J. Phys. Chem. 28, 984 (1924).

[2] J. Am. Chem. Soc. 43, 53 (1921).

[3] White and Tolman; J. Am. Chem. Soc. 47, 1240 (1925); Hirst: J. Chem. Soc. 127, 657 (1925).

[4] Rideal and Taylor: Catalysis in Theory and Practice; Taylor: "Treatise on Physical Chemistry", Chap XV.

[5] "Treatise on Physical Chemistry", p. 1212.

Weigert[4] has shown that a number of gas reactions can be sensitized to light in a spectral region easily available. By the addition of chlorine to the reaction mixture, he has studied the decomposition of ozone and the combination of hydrogen and oxygen in visible light.

One must remember that in all photochemical gas reactions conditions are considerably simplified over those obtaining in purely thermal reactions. The reactions are homogeneous and the method of activation is known. If the primary action of the light can be interpreted it is usually possible to obtain a fairly complete idea of the mechanism of the reaction.

A large number of workers, since the time of Davy, have investigated the thermal reaction between hydrogen and oxygen. This work has clearly shown that the controlling influence for this reaction is the nature of the surface exposed, the reaction being hetereogeneous. Bodenstein[5] has investigated the reaction over a glazed porcelain surface in the temperature range 482°-689°C and at ordinary temperatures with a platinum catalyst. Bone and Wheeler[6] have made a very complete study with a large variety of catalytic material and have demonstrated that the reaction depends primarily on the condensation of one or the other of the reactants on the heated surface. Langmuir[7] has shown that with platinum as a catalyst in the temperature range 300°-600°K the reaction velocity is proportional to the oxygen pressure and inversely to that of the hydrogen. He interprets this as meaning that adsorbed oxygen atoms on the platinum surface are very reactive towards hydrogen, every collision between a hydrogen molecule and an oxygen atom resulting in combination. Under certain conditions, he states, adsorbed hydrogen atoms are relatively inactive towards oxygen molecules.

Direct photochemical investigation of this reaction is very difficult since oxygen does not commence to absorb appreciably above 195$\mu\mu$ and hydrogen is diactinic down to 103$\mu\mu$. Any photochemical reaction observed must be due to activation of the oxygen present. Andreew[8] has observed that under the influence of ultraviolet light the rate of reaction is independent of the concentration of the reacting gases. Coehn and Grote[9] have studied this reaction in the temperature range 150°-240°C. They obtain a velocity constant of the first order from their kinetic studies. Also they report a trace of hydrogen peroxide in the initial stages of the reaction. The temperature coefficient is given as 1.04. They put forward a reaction mechanism of the type

---

[1] Z. physik. Chem. **114**, 208 (1924).

[2] Christiansen: Dansk. Vid. Math. Phys. Med. **1**, 14 (1919); Polanyi; Z. Elektrochem. **26**, 50 (1920); Herzfeld: **25**, 301 (1919).

[3] Bodenstein and Lind: Z. physik. Chem. **57**, 118 (1906).

[4] Ann. Physik, (4) **24**, 55, 243 (1907).

[5] Z. physik. Chem. **29**, 665 (1899).

[6] Phil. Trans. **206A**, 1 (1906).

[7] Trans. Faraday Soc. **17**, 621 (1921).

[8] J. Russ. Phys. Chem. Ges. **43**, 1342 (1911).

[9] "Nernst Festschrift", p. 136.

$$H_2 + O_2 = H_2O_2$$
$$H_2O_2 + H_2 = 2H_2O$$

Weigert[1] has observed that the reaction can be sensitized by chlorine and Norrish and Rideal[2] have investigated this reaction in detail and suggested a possible mechanism. The reaction is completed by the formation of hydrogen chloride but they have shown that the rate of reaction is independent of the hydrogen concentration and can be represented by the equation

$$\frac{d[H_2O]}{dt} = K\,[Cl_2]\,[O_2]$$

Griffith and Shutt[3] have studied the photochemical reaction between hydrogen and ozone-oxygen mixture in visible light. They find that the presence of hydrogen causes the reaction

$$2O_3 \longrightarrow 3O_2$$

to take place many times faster. In a mixture 6% O_3, 40% H_2, 54% O_2 it goes five times as fast as in the absence of hydrogen. The secondary reactions may be either

$$O + H_2 \longrightarrow H_2O \quad \text{or}$$
$$O_3\ (\text{activated}) + H_2 \longrightarrow H_2O + O_2$$

depending on the mechanism postulated for the primary action of the light. They suggest some sort of a chain mechanism involving energy-rich water molecules to explain the effect of the hydrogen.

Taylor and Marshall[4] have observed that a large number of hydrogenation reactions will proceed in the gas phase when the mixture contains mercury vapor and is illuminated by the light of a cold mercury arc. This paper will give an account of a more complete investigation of the reaction between hydrogen and oxygen. The method of sensitization by mercury has already been described. In our previous experiments a pressure decrease of thirty millimeters per hour was the maximum rate observed.

The apparatus now to be described was designed to enable one to utilize completely all the radiation, from the quartz mercury arc, that is absorbable by mercury vapor. A compartment for a light filter has been provided and it is possible to control the temperature of the reaction system independently from that of the arc. A diagram of the cell is given in Fig. 1. The inner compartment contains the quartz mercury arc C which is cooled by a flow of tap water from A to B; electrical connections are made as indicated. The compartment D is evacuated and enables one to control the temperature of E and F independently from C. The compartment E is 6 mm. in thickness and in some of the experiments contained chlorine at two atmospheres pressure together with about 60 mm. pressure of bromine. The compartment F is 55 mm. inside diameter and 71 mm. outside giving a thickness of 6 mm; it is 100 mm. long. The capillary G connects to gas holders and a manometer. The whole apparatus was placed in a thermostat to give accurate temperature control. The arc is 90 mm. long between the tungsten spiral and the mercury surface and is centered in the tube by quartz lugs fused to it.

---

[1] Ann. Physik, (4) **24**, 55, 243 (1907).
[2] J. Chem. Soc. **127**, 787 (1925).
[3] J. Chem. Soc. **123**, 2752 (1923).
[4] J. Phys. Chem. **29**, 1140 (1925).

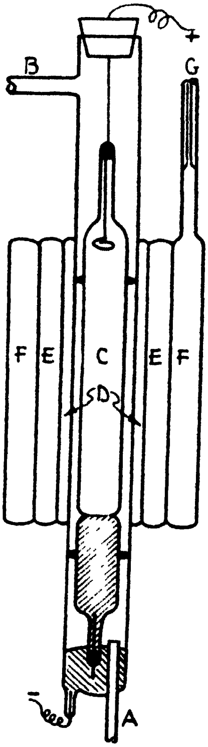


Fig. 1

Wood[1] gives the following table for the relative intensity of the lines in the cold mercury arc.

TABLE I

Relative Intensities of Lines in Cold Mercury Arc

λ	Intensity	λ	Intensity
2536	400	3131	50
2652	8	3341	8
2753	2	3650	64
2805	1	3654	30
2894	4	3663	30
2967	12	4046	100
3023	10	4077	30
3125	30	4358	200
		5461	400

The chlorine-bromine light filter absorbs all the radiation in the range 2900–5000 A° so that apart from the yellow and green lines the only light of any intensity reaching the vessel is 2536 A° which is the wave length employed.

The volume of the reaction chamber was about 120 c.c. and the capillary connecting to the manometer which was external to the thermostat has a volume of 2 c.c. Experiments were carried out in the temperature range 25—70°C. The hydrogen and oxygen were prepared electrolytically, passed over heated palladized asbestos and dried over phosphorous pentoxide. In some cases the mixtures used were prepared directly by electrolysis by the use of auxiliary electrodes. This ensured complete mixing before introducing into the reaction chamber. This factor was of importance since the reactions proceeded so rapidly. Some seventy-five experiments in all have been performed and the results of these will be given in a series of tables and curves.

A number of experiments at 50°C with gas mixtures ranging in composition from 406 mm. H_2 and 148 mm. O_2 to 572 mm. H_2 and 156 mm. O_2 gave reactions taking place at the same rate, the pressure decrease being 24.7 mm.

---

[1] Proc. Roy. Soc. **106A**, 679 (1924).

per minute. The pressure-time curves showed an initial break at a point corresponding to saturation with water vapor and the curve was then linear till the reaction was complete, the rate thus being independent of the total pressure to a partial pressure of hydrogen or oxygen of the order of a few millimeters. In all these cases there was an excess of hydrogen over the amount required to combine with all the oxygen present. Fig. 2 (a) illustrates the type of curve obtained. The curves were quite different in character when oxygen was present in excess. The rate of combination decreased rapidly as the reaction proceeded. Typical results are given in Fig. 2 (b) and (c).

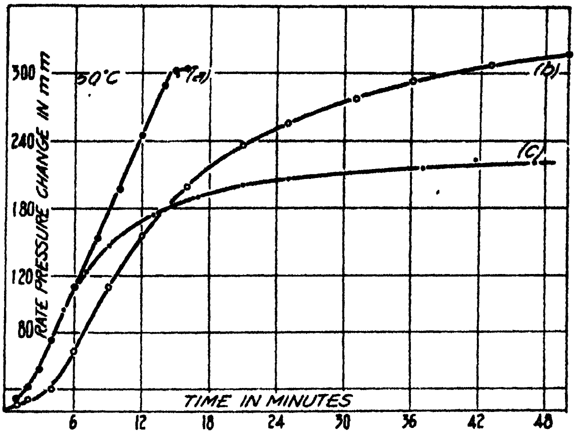


FIG. 2

The Compositions of the Reacting Mixtures are

(a) 520 mm H_2
131 mm O_2
(b) 294 mm H_2
481 mm O_2
(c) 208 mm H_2
229 mm O_2

A large number of experiments were made with mixtures containing approximately two volumes of hydrogen to one of oxygen in the temperature range 25°–70°C. Table II summarizes these results. The rate of pressure change was that determined after saturation had been reached.

TABLE II

Temperature	Rate of Pressure Change mm./min.
50°	38.3
60°	45
70°	48

Table III gives similar results where the experiments had been sandwiched in order to obtain some idea of the reproducibility of the results. The numbers in brackets give the order in which the experiments were performed.

TABLE III

Temperature	60°	40°	25°
	36.8 one		
		18.6 two	
			2.72 three
	39.0 four	24.0 five	
		25.7 six	

In the first five of these experiments a chlorine-bromine light filter was used. For experiment (6) this was removed and the results show that it exerted no appreciable influence.

The results in these two tables indicate that the temperature coefficient obtained in this way is a very involved quantity. There seem to be at least two factors entering; firstly the increased vapor pressure of mercury at the higher temperatures giving an increased light absorption and secondly the increased yield per quantum absorbed. Table IV gives the vapor pressures of mercury in the temperature range under consideration.

TABLE IV

Vapor Pressures of Mercury

Temperature	Vapor Pressure
25	.0017 mm.
40	.0057 "
50	.012 "
60	.025 "
70	.06 "

From the measurements given by Wood[1] on the extinction coefficient of mercury vapor for λ2536.7 A° it appears that at temperatures slightly above 25° there should be complete absorption. These values however were obtained for pure mercury vapor. Later results by the same author[2] indicate that the presence of other gases may greatly modify the width of the absorption band and very probably the magnitude of the extinction coefficient as well. In pure helium at 14 cm. pressure and room temperature the resonance radiation is enormously enhanced and the width of the line is broadened. Wood estimated a thirty fold increase in intensity. From this work it is evident that it will be necessary to obtain exact experimental evidence on the quantum yield at the various temperatures before any definite evidence can be given on the temperature coefficient of this reaction. The fact that the values at 60° and 70° agree so closely seems to indicate that the true temperature coefficient will be found to be very close to unity. Another complication enters at the higher temperatures from the fact that the reaction mixture cannot be completely homogeneous. The energy absorption will be very high at the inner surface of the reaction vessel and decrease rapidly as the light progresses thru the chamber. Hence the rate of reaction will be different in various parts of the vessel and this will cause concentration differences to be set up.

---

[1] Phil. Mag. **23**, 689 (1912).

[2] Wood: Proc. Roy. Soc. **106**, 674 (1924).

At the end of experiment (28) the apparatus was dismantled and the reaction chamber was found to be heavily coated with yellow mercuric oxide. This will undoubtedly account for some of the variability in rate between successive experiments. It was later observed that the mercuric oxide was formed to the greatest extent in experiments using excess of oxygen and more particularly towards the end of these runs. This point will be discussed in more detail later. Another factor of importance in causing variability is the gradual deterioration of the quartz mercury arc. In later experiments with a new arc rates twice as great as those mentioned so far were obtained.

Fig. 3 illustrates some of the results obtained in later experiments. In these cases the reaction mixture ($2H_2:1\,O_2$) was prepared by direct electrolysis of caustic soda solution and dried over phosphorous pentoxide. The reaction proceeded at a constant rate until the very end, the final pressure in every case being the vapor pressure of water at the temperature of the experiment. Table V gives a more complete list of the experiments. The experiments are numbered in the order of their occurrence. Experiments 1–9 and 10–32 were carried out on consecutive days. After experiments 21, 23, 25, 27, 28 and 30 pure hydrogen was admitted to the reaction chamber and illuminated for about half an hour in order to remove any mercuric oxide from the vessel walls. After experiment 31, the vessel was thoroly cleaned. From these experiments it is evident that a considerable portion of the variability is due to the coating of mercuric oxide on the walls, which apparently cuts down the transmission of the active radiation.

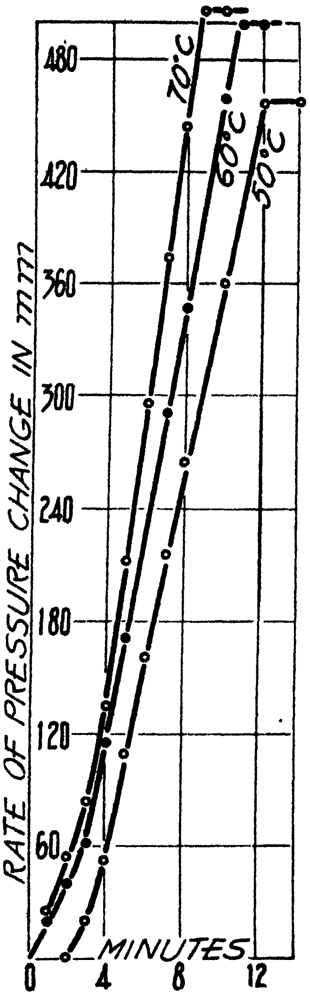


FIG. 3

Figs. 4 and 5 illustrate experiments with mixtures containing approximately equal amounts of hydrogen and oxygen. Tangents have been drawn to these curves at a number of points to determine the rate at these points. Table VI presents the values obtained. The first column gives the H_2 pressure in mm., the second the oxygen, the third, fourth and fifth the ratios H_2/O_2, $H_2/(H_2 + O_2)$ and $H_2/(H_2 + O_2 + H_2O)$ the sixth the rate of reaction in

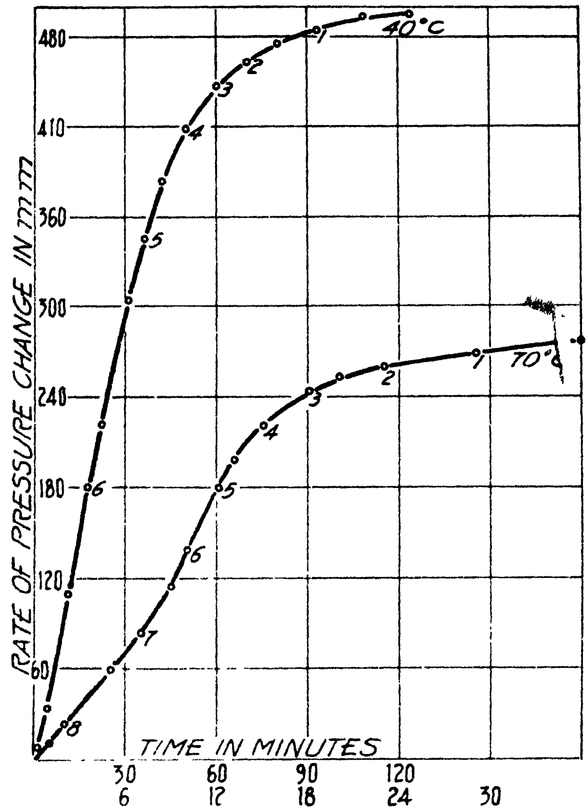


FIG. 4

Composition of Gas
40° = 359 mm H_2, 364 mm O_2
70° = 336 mm H_2, 341 mm O_2

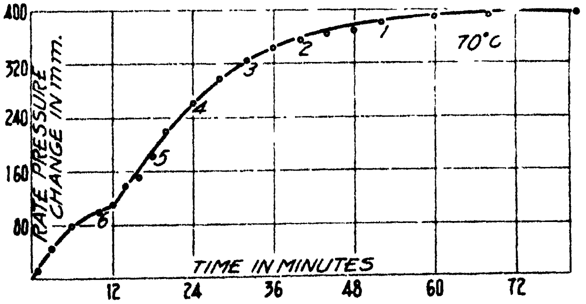


FIG. 5

TABLE V

Rate of Reaction in mm./ min.

Temperature	70°	60°	50°	40°	25°
		67.3 (2)		51.1 (1)	
		80.0 (3)			
		85.0 (4)	71. (6)		14.9(5)
	87.2 (8)		77.5 (7)		
	86.4 (9)				
	77.5 (10)				
	79.0 (11)				
	77.5 (12)				
	72.4 (13)				
	71.4 (14)			43 (15)	
				32.1 (16)	
				28 (17)	
		57 (18)			
		51.1 (19)			
		52.6 (20)			
	57.8 (21)				
	73 (22)				
	65.6 (23)	70 (24)			
	65 (27)	65.2 (25)		35.3 (26)	
	57.2 (31)		47.9 (29)	41.5 (28)	
	70 (32)		50.5 (30)		

mm. pressure change per minute and the remaining columns this rate divided by the above ratios.

The numbers in brackets refer to the points on the curves in Figs. 4 and 5. The last three columns give the constants for the kinetic equations

$$\frac{d[H_2O]}{dt} = K_1 \frac{[H_2]}{[O_2]} \qquad (1)$$

$$= K_2 \frac{[H_2]}{[H_2] + [O_2]} \qquad (2)$$

$$= K_3 \frac{[H_2]}{[H_2] + [O_2] + [H_2O]} \qquad (3)$$

The degree of constancy is about the same in each case so that the data from this type of experiment with excess of oxygen will not permit us to differentiate between these three equations. The method used to determine the hydrogen pressure—calculation from point to point on the curve assuming no side reactions—makes all the errors cumulative. It is proposed to repeat these experiments with a modified apparatus, employing a circulatory system which will enable samples to be taken from time to time during the course of the reaction. This will enable one to obtain a much more accurate idea regarding

TABLE VI

70°C (Fig. 4)

H_2	O_2	H_2/O_2	$H_2/H_2 + O_2$	$H_2/H_2 + O_2 + H_2O$	Rate	$\frac{\text{rate}}{H_2/O_2}$	$\frac{\text{rate}}{H_2/H_2 + O_2}$	$\frac{\text{rate}}{H_2/H_2 + O_2 + H_2O}$
(2) 10.6	178	.059	.056	.025	1.9	32	34	76
(3) 21.2	184	.115	.103	.048	5.3	46	51	110
(4) 36.5	191	.19	.16	.079	9.4	49	59	119
(5) 64	205	.31	.24	.127	18	58	75	140
(6) 93	219	.42	.29	.17	22	52	76	130
(7) 150	248	.61	.37	.24	32	53	87	130
(8) 271	308	.88	.47	.43	37	42	79	86
40°C (Fig. 4)								
(1) 6.6	187	.035	.034	.026	0.65	18	19	26
(2) 22	195	.113	.101	.081	1.4	12	14	17
(3) 32	200	.16	.14	.11	2.1	13	15	19
(4) 52	210	.25	.20	.16	3.6	14	18	23
(5) 100	234	43	.30	.26	7.3	17	24	28
(6) 144	256	.56	.36	32	10	18	28	31
70°C (Fig. 5)								
(1) 10	195	.051	.049	.023	1.2	24	25	52
(2) 26.6	203	.13	.115	.057	2.7	21	24	47
(3) 47	214	.22	.18	.094	5.6	26	31	60
(4) 90	235	.38	.28	.16	9.0	24	32	56
(5) 141	260	.54	.35	.22	13	24	37	59
(6) 196	288	.68	.40	.30	16	24	40	54

the value of K. The degree of constancy obtained is all one can expect under present conditions.

The results obtained at the higher temperature with the $2H_2 + 1O_2$ mixtures seem to rule out equation (3). In these cases the water vapor pressure was as high as 250 mm. but in no case did the reaction rate show any decrease until the very end. Some of the earlier experiments at 50°C using excess hydrogen over that necessary for a two to one mixture showed practically no increase in rate towards the end of the reaction as predicted by equation (1). So it can be said that the results at present available favor the kinetic equation (2).

$$\frac{d\,[H_2O]}{dt} = K_2 \frac{[H_2]}{[H_2] + [O_2]}$$

Experiments by H. A. Stuart[1] on the quenching of resonance fluorescence in mercury vapor by various gases indicate that hydrogen, oxygen and water vapor all have a very strong effect in quenching the fluorescence. In the light of this knowledge, it seems that these gases are all able to take energy from excited mercury atoms by collisions of the "second kind," and in amounts proportional to their concentration. Cario and Franck[2] have shown that hydrogen atoms are formed by collisions between molecular hydrogen and excited mercury molecules. Apparently the energy absorbed by the oxygen is degraded as heat. The probability of the collision of a hydrogen molecule with an excited mercury atom is proportional to the hydrogen pressure divided by the sum of the hydrogen and oxygen pressures and it is this probability which determines the rate of the reaction.

It is possible to put forward several suggestions concerning possible mechanisms but the thermal data are entirely lacking to test these thermodynamically. The first step is of course the dissociation of hydrogen then

$$\begin{array}{lll}
H_2 + Hg\ (\text{excited}) & = 2H + Hg & (1)\\
H + O_2 & = HO_2 & (2)\\
HO_2 & = HO + O & (3)\\
HO_2 + H_2 & = H_2O_2 + H & (4)\\
O + H_2 & = H_2O & (5)\\
OH + H_2 & = H_2O + H & (6)\\
H_2O_2 & = H_2O + O & (7)
\end{array}$$

Such a series of reactions would give a "chain mechanism." If (4) is one of the steps in the reaction it should be possible by use of a rapid circulatory system to remove the hydrogen peroxide from the reaction chamber and obtain sufficient quantities for a qualitative test. There is a distinct possibility also of ozone taking part in the reaction. If hydroxyl is present in one stage it might be possible to show its presence by a study of the reactions in a mixture of ethylene, hydrogen and oxygen. There is one other possible factor that has not been discussed so far. There is at present no experimental evidence on the intensity of the 1849 A° line in the water cooled arc altho Wood[1] has evidence of its presence. This light also excites resonance radiation, of greater energy, in mercury and the quantum (150 Kg. cals.) may be sufficient to dissociate oxygen. Further work will be necessary to settle this point.

---

[1] Z. Physik, 33, 262 (1925).

[2] Z. Physik, 11, 162 (1922).

It has been mentioned that at times considerable amounts of mercuric oxide are formed. The rate of formation is greatest at 70°C, where there is a relatively high concentration of mercury vapor. A high mol fraction of oxygen greatly favors its formation. Under these conditions it is possible for the reaction

$$Hg + O = HgO$$

to proceed to a considerable extent and this may be the mechanism of its formation.

A very rough calculation shows that a considerable portion of the energy of λ 2536 emitted by the arc must be absorbed in the reaction system to obtain equivalence between quanta absorbed and molecules reacting. The lamp was burning on 20 volts and 10 amps. The intensity of the visible radiation is very much less than with the arc burning at 60 volts and 3 amps. Let us assume that 10% of the energy, some 20 watts is radiated and that 25% of this is in the 2536 A° line. This amounts to 5 watts with a quantum of 7.8 $(10)^{-12}$ ergs or 3.8 $(10)^{20}$ quanta. The maximum rate observed was 8 cm. pressure change per minute in a volume of 120 c.c. which corresponds to

$$2/3 \times 8/760 \times 120/22400 \times 6\ (10)^{23} = 2.2\ (10)^{19}$$

molecules of water formed per minute.

This calculation shows that it is necessary for large absorption of the 2536 A° line to obtain equivalence. Unless the width of the absorption band of mercury is very greatly increased by the presence of the reacting gases such equivalence is impossible. In a previous communication[2] it has been pointed out that the reaction between hydrogen and ethylene does not take place when the mixture is illuminated by a hot mercury arc. This is attributed to self-reversal of the resonance line in the arc. Such reversal, however, cannot be detected with an ordinary quartz spectrograph. This seems to indicate that in this case at least only a very small fraction of the energy in the line 2536 A° is useful in exciting the mercury atoms. At present it seems necessary to postulate a "chain mechanism," such as that given, to account for the rate of reaction observed.

Summary

Photochemical studies of gas reactions should yield valuable information on the mechanism of chemical reactions.

---

[1] Proc. Roy. Soc. **106**, 687 (1924).

[2] This Journal **29**, 1140 (1925).

A quartz reaction system has been developed to study reactions sensitized by optically excited mercury atoms.

A more complete study of the reaction between hydrogen and oxygen has been made. The kinetic equation has been shown to be of the form

$$\frac{d[H_2O]}{dt} = K \frac{[H_2]}{[H_2] + [O_2]}$$

It seems probable from energy considerations that we are dealing with a "chain reaction" and several possible mechanisms are advanced.

Research Laboratory
General Electric Company
Schenectady
New York

THE HEAT CAPACITIES OF SOME METALLIC OXIDES

BY GEORGE S. PARKS AND KENNETH K. KELLEY

The past fifteen years have witnessed a rather extensive study of the heat capacities of substances at low temperatures. In this connection the elements themselves and certain classes of compounds, notably the halogen salts, have been investigated to a considerable extent. On the other hand, only scanty data on metallic oxides have been published, although such information is of importance from both the theoretical and the industrial standpoint. In view of this situation, about two years ago there was initiated in this laboratory a systematic investigation of the heat capacities of oxides at low temperatures. The present paper records the results of measurements made upon the oxides of magnesium, calcium, and aluminum and upon the two iron compounds, hematite and magnetite.

Experimental Part

Method.—The method was essentially the same as that recently employed by one of us[1] in an investigation of the specific heats of aliphatic alcohols.

In every case the sample of oxide studied was either in the form of a powder or of small crystals, never exceeding 3 or 4 mm. in dimensions. Such a sample was placed in a gas-tight, cylindrical copper can, 8 cm. long and 2.5 cm. in diameter, with a capacity of approximately 40 cc. To facilitate the attainment of thermal equilibrium the inside of this container was fitted with perforated disks, spaced 2 to 4 mm. apart along a small copper tube which ran through the center of the cylinder and served as a holder for the thermocouple used in measuring the temperatures. These disks, even though made out of extremely thin copper foil, added considerably to the weight of the calorimeter; their use, however, was justified by the fact that in this way no portion of the oxide under investigation was more than 2 mm. from a highly conducting copper surface. A 150-ohm heating coil made from B. and S. No. 36, silk-insulated Therlo wire was wound around the outer surface of the can and baked on with electricians' enameling fluid; it had external leads of No. 40 copper wire. To reduce heat losses through radiation thin silver foil was then wrapped tightly around the container. The bottom of the can, sealed in with soft solder and easily removable, provided a means of introducing and removing the sample of oxide. The finished calorimeter, constructed with these features, weighed about 35 grams. Its heat capacity in the unfilled state represented, on the average, about a quarter of the total heat input during a specific heat determination on the oxides and was measured in a separate series of experimental runs.

The calorimeter was suspended by silk thread within a larger copper cylinder weighing about 600 gm. This sheath, fitted with a top and bottom and silvered on both its inner and outer surfaces, provided a relatively uniform temperature environment for the heat capcity determinations. In order to control its temperature it was equipped with a heating-coil and thermocouple. The cylinder and contents rested on small wooden legs in a vacuum-tight brass can, 5 cm. in diameter and 15 cm. high. A German-silver tube 1 cm. in diameter and 50 cm. long, soldered into a hole in the top of the brass can, served the three-fold purpose of connecting the system to the charcoal evacuating tube, of providing an exit path for the electrical connections and of serving as a support, the entire apparatus being suspended in a 1000 cc. Dewar jar. Details of electrical wiring, bringing out the connections, etc. were similar to those recently described by Rodebush[1] in his work upon cadmium and tin and will not be repeated here.

---

[1] Parks: J. Am. Chem. Soc., **47**, 338 (1925).

A satisfactory vacuum was obtained by a preliminary evacuation with a Nelson oil-pump, followed by the use of activated charcoal immersed in liquid air. The desired temperatures were attained with the aid of various baths such as liquid air, crystalline ethyl alcohol (melting point, 158° K.), solid carbon dioxide in alcohol, ice, and water at approximately the temperature of the room.

Single-element copper-constantan thermocouples, constructed from B. and S. No. 40 silk-insulated copper and No. 30 silk-insulated constantan wire were used with a White potentiometer in measuring the temperatures of the calorimeter and copper sheath. For these thermocouples the temperatures and the rates of change of e. m. f. with change of temperature, dE/dT, were obtained by means of the two equations of Eastman and Rodebush,[2] since the wire used was evidently similar to theirs. From a careful study of this Eastman-Rodebush temperature scale we have concluded that its use involves an error of less than 0.2% above 200° K. and probably not more than 0.5% in any region below this point.

The actual procedure in making the measurements was as follows. The system was first evacuated and an appropriate bath was placed around the external brass can. When the calorimeter and surrounding copper sheath had attained the desired temperature (a process which often required a day or more in the case of the lower temperatures), the reading of the calorimeter thermocouple was carefully recorded. Heat was then supplied to the calorimeter for a period of four to eight minutes by means of an electric current from an 8-volt storage battery. During this interval the energy input was measured with an accuracy of 0.1% by a calibrated stop-watch and a potentiometric evaluation of the current and voltage. In general it was such as to cause a temperature rise of about 4°. After switching off the heating current, the readings of the calorimeter thermocouple were recorded at one minute intervals for about half an hour. As a rule a very regular cooling rate was attained within the first four to six minutes of this period, indicating that heat equilibrium had been reached. The remaining thermocouple readings sufficed for an accurate evaluation of the cooling correction during and immediately following the heating period. This correction was but a small percentage of the total temperature rise.

---

[1] Rodebush: J. Am. Chem. Soc., **45**, 1413 (1923).

[2] Eastman and Rodebush: J. Am. Chem. Soc., **40**, 492 (1918).

As a typical example of the way in which the results were obtained, the calculations from the data for one of the magnesium oxide runs are given in detail.

Time, 361.4 seconds.
Voltage at terminals of heating coil, 7.958 volts.
Current through heating coil, 0.05270 amperes.
Total heat supplied, (361.4) (7.958) (0.05270) (.2391) = 36.250 cal.
Initial thermocouple reading, 5586.1 microvolts
Final thermocouple reading, corrected for cooling, 5449.3 microvolts
Difference 136.8 "
Temperature corresponding to average thermocouple reading, 94.1° K.
Corresponding dE/dT, 19.63 microvolts
Heat supplied to calorimeter and contents per degree,

$$36.250\ (19.63 \div 136.8) = 5.201 \text{ cal.}$$

Heat capacity of calorimeter at 94.1° K., 2.130 cal.
Heat supplied to magnesium oxide per degree,

$$5.201 - 2.130 = 3.071 \text{ cal.}$$

Weight of magnesium oxide, 76.40 gm.
C_p of magnesium per gram, 3.071/76.40 = .0402 cal.
C_p per mean gm. atom, 0.81 cal.

Materials

Magnesium Oxide.—A high-grade sample of fused magnesium oxide was employed. On examination it gave no tests for any of the common impurities, such as silica or calcium, and seemed to be 100% pure within the limits of analytical error. It had been given to Professor D. L. Webster of the Physics Department of Stanford University by the Norton Company.

Calcium Oxide.—Kahlbaum's calcium oxide was used. An analysis of this material gave 98.8% CaO, 0.4% H_2O and no SiO_2.

Aluminum Oxide.—Small, almost colorless sapphires from Ceylon were employed in the measurements. An analysis made upon them gave 99.3% Al_2O_3.

Ferric Oxide.—Two samples of ferric oxide were studied. The first, consisting of large crystals of specular hematite from the Island of Elba, gave on analysis 99.2% Fe_2O_3, 0.5% H_2O and 0.5% SiO_2.

The second sample was Kahlbaum's product, prepared from the oxalate. It gave 99.5% Fe_2O_3, the remaining 0.5% being presumably moisture. This material consisted of a fine, smooth powder and on X-ray analysis[1] yielded much fainter lines than did a powered crystal of the specular hematite. A rough estimate of the relative intensities would place them, perhaps, in the ratio of 1 to 10. Apparently, then, this Kahlbaum sample contained a large amount of amorphous substance.

---

[1] For advice and assistance in making this X-ray analysis, the authors wish to acknowledge their great indebtedness to Professor P. A. Ross of the Physics Department of Stanford University.

Magnetite.—The magnetite used was similar to that employed by Sosman and Hostetter[1] in an earlier investigation and was in the form of remarkably perfect, large crystals. The Sosman-Hostetter analysis gave 99.00% Fe_3O_4 0.63% Fe_2O_3, and 0.37% impurities (chiefly quartz.)

Heat Capacity Data

The results of the measurements appear in Tables I-VI inclusive. In each case the first column contains the temperatures in degrees absolute; in the second column appear the corresponding heat capacities at constant pressure per gram of the material and in the third column are the resulting values for the mean atomic heat. These specific and atomic heats are expressed in terms of the 15° C. calorie, which is used throughout the present paper.

As to the accuracy of the results, it is very hard to state definitely. In general the measurements themselves are reproducible to 0.5% or better and probably in no region of the temperature scale involve an absolute error of more than 1.0%. On the other hand, the impurities, which in certain instances are of the order of 1%, may affect the results to some extent, although the magnitude of their influence is rather problematical. For this reason no attempt to correct for the effect of impurities has been made is presenting the data.

In the studies with magnetite a region of marked heat absorption was noted in the short temperature interval, 113°-117° K. A rough measurement of this heat effect gave 0.69 cal. per gram or 23 cal. per mean gram atom. In the case of no other substance was a heat absorption or transition point observed.

TABLE I

The Heat Capacity of Magnesium Oxide

Temperature °K	C_p per gram	C_p per gram atom
94.1	0.0402	0.81
97.9	0.0442	0.89
98.5	0.0450	0.91
100.0	0.0470	0.95
151.8	0.1101	2.22
188.4	0.1452	2.93
193.4	0.1502	3.03
275.3	0.2096	4.22
278.0	0.2137	4.30
288.3	0.2170	4.37
291.0	0.2184	4.40

---

[1] Sosman and Hostetter: J. Am. Chem. Soc., 38, 812 (1916). Dr. Sosman very kindly loaned us this material for our investigation.

TABLE II

The Heat Capacity of Calcium Oxide

Temperature °K	C_p per gram	C_p per gram atom
87.2	0.0535	1.50
87.7	0.0536	1.50
91.1	0.0579	1.62
92.2	0.0591	1.66
150.3	0.1158	3.25
194.0	0.1446	4.06
197.1	0.1474	4.13
275.4	0.1762	4.94
277.8	0.1772	4.97
282.1	0.1794	5.03
292.7	0.1808	5.07

TABLE III

The Heat Capacity of Aluminum Oxide

Temperature °K	C_p per gram	C_p per gram atom
91.1	0.0249	0.51
91.7	0.0255	0.52
93.0	0.0260	0.53
95.6	0.0286	0.58
150.6	0.0768	1.57
193.3	0.1155	2.35
197.2	0.1190	2.43
200.1	0.1218	2.48
275.1	0.1726	3.52
276.4	0.1743	3.55
288.6	0.1800	3.67
291.3	0.1813	3.70

TABLE IV

The Heat Capacity of Ferric Oxide (Specular)

Temperature °K	C_p per gram	C_p per gram atom
89.8	0.0404	1.29
90.3	0.0414	1.32
90.5	0.0410	1.31
95.5	0.0445	1.42
148.4	0.0827	2.64
186.9	0.1082	3.46
192.8	0.1109	3.54
196.3	0.1128	3.60
275.9	0.1477	4.72
278.1	0.1488	4.75
289.1	0.1534	4.90
291.9	0.1539	4.92

TABLE V

The Heat Capacity of Ferric Oxide (Kahlbaum's)

Temperature °K	C_p per gram	C_p per gram atom
88.3	0.0412	1.32
91.8	0.0442	1.41
95.2	0.0465	1.48
98.3	0.0485	1.55
150.3	0.0858	2.74
194.3	0.1141	3.65
198.5	0.1162	3.71
274.9	0.1521	4.86
276.7	0.1529	4.88
286.9	0.1551	4.96
289.4	0.1561	4.99

TABLE VI

The Heat Capacity of Magnetite

Temperature °K	C_p per gram	C_p per gram atom
90.0	0.0488	1.61
90.2	0.0493	1.63
94.2	0.0524	1.73
96.9	0.0550	1.82
153.2	0.0968	3.20
193.5	0.1186	3.92
197.2	0.1205	3.99
276.3	0.1513	5.00
278.7	0.1525	5.04
292.1	0.1558	5.15
295.0	0.1570	5.19

Discussion of Results

The preceding data possess several interesting features. One of these pertains to the relatively low mean atomic heat for Al_2O_3 in the sapphire form. At the temperature of liquid air this falls to 0.5 cal. per atom or 2.5 cal. per formula weight, a rather striking figure in view of the fact that the heat capacity of two atoms of metallic aluminum plus that of three atoms of liquid oxygen amounts to about 24.0 cal. at 90° K. Certainly this situation constitutes an excellent confirmation of the very general view that a low heat capacity is a concomitant of exceptional hardness, as corundum ranks No. 9 on the Mohr scale of hardness where diamond has the maximum value of 10.

The two samples of ferric oxide studied are approximately of the same purity, the essential difference being in the degree of subdivision. Throughout the entire temperature range the Kahlbaum powder was found to have a higher specific heat than the specular crystals, the excess amounting to 2.4% at 275° K. and 3.8% at the temperature of liquid air. Now these percentage differences, while small, we believe to be greater than any that would probably result from the experimental errors in the two sets of determinations. Therefore, in our opinion these results indicate that a powder which is finely divided and somewhat amorphous possesses a higher heat capacity than large crystals of the same chemical composition.

The heat absorption, found in the case of the magnetite crystals at about 115° K., constitutes still another noteworthy feature. This temperature would seem to be very low for a transformation in crystal structure in a metallic oxide, the melting-point of which is above 1500° K. Moreover, after the runs the large crystals of magnetite showed no signs of alteration or disintegration, such as might conceivably be expected after a series of alternations in crystal structure. In view of these considerations we think that the observed heat effect may possibly be connected with a change in the magnetic properties of the substance. If this be the case, there might be no change in crystal structure, as Compton and Rognley[1] have failed to detect such a change in a magnetite crystal upon magnetization and demagnetization. Certainly this heat absorption phenomenon should be investigated further.

Entropies of the Oxides.—If we assume the validity of the third law of thermodynamics as stated by Lewis and Gibson[2], all the crystalline oxides have zero entropy at 0° K. The atomic heat values then provide a basis for a quantitative estimate of the entropies of the same substances at 298° K. or 25° C.

In a careful study of heat capacity data Lewis and Gibson[3] have shown that for a number of substances the atomic heat capacities at constant volume are expressible as functions of the absolute temperature by the equation,

$$C_v = f\left(\frac{T}{\Theta}\right)^n,$$

in which f is the same function for all substances and Θ and n are characteristic constants for each particular substance. For many substances crystallizing in the cubic system and for a number of monatomic elements, n is equal to unity (Class I). For other substances n is less than unity (Class II).

Of course in the present investigation our experimental values are for C_p rather than C_v but for the oxides the differences between these two quantities are relatively small at room temperature and become entirely negligible at lower temperatures.[4]

---

[1] Compton and Rognley: Phys. Rev., **16**, 464 (1920).

[2] Lewis and Gibson: J. Am. Chem. Soc., **42**, 1533 (1920).

[3] Lewis and Gibson: J. Am. Chem. Soc., **39**, 2565 (1917).

[4] In the case of magnesium oxide there are data which permit us to calculate these differences between C_p and C_v. Utilizing the values for the coefficients of compressibility and thermal expansion tabulated by Pease (Taylor: "Treatise on Physical Chemistry", p. 171 (1924)), we have calculated C_p-C_v at 293° K. by the thermodynamic equation used by Lewis: J. Am. Chem. Soc., **29**, 1165 (1907).

$$C_p - C_v = .0242 \frac{\alpha^2 VT}{\beta}$$

This difference was found to be 0.04 cal. per gram atom. The empirical rule expressed by Lindemann and Magnus (Z. Elektrochem., **16**, 269 (1910)) in the equation,

$$C_p - C_v = aT^{3/2}$$

then gives 0.01 cal. for $C_p. - C_v$ at 100° K.

Accordingly, on plotting our results for C_p we have found that the data for the oxides of magnesium and calcium, the two compounds which possess a cubic structure like that of sodium chloride, agree well with the C_v curve for solids of Class I. Fig. 1 shows this clearly for MgO. On the other hand, the data for the remaining oxides require a slightly flatter curve at the lower temperatures, where the experimentally determined heat capacities appear to approximate the requirements for a substance of Class II with a value of about 0.9 for n. Whether the "n formula" in these cases is more than a first approximation is, however, extremely doubtful. Its application nevertheless will involve only small absolute errors in instances, like the present, where the total entropy of each substance is small at the temperature of liquid air.

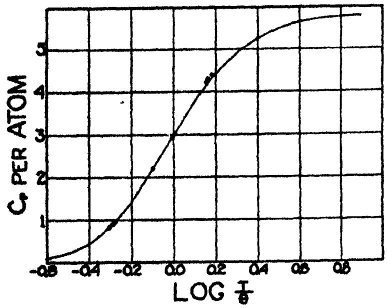


Fig. 1

C_p Values for MgO and the Lewis-Gibson Curve for Class I.

Following in detail the methods of Lewis and Gibson, we have obtained the results which are given in Table VII. The entropy value for Fe_2O_3 is that found for the specular crystals; for the Kahlbaum powder our estimate is at least 0.4 cal. per degree above this figure. The result for magnetite includes the entropy change of 1.4 units at the heat-absorption point previously referred to.

Table VII

Entropies of the Oxides per Formula Weight at 298°K.

Substance	log θ	n	Entropy in cal./degree
MgO	2.28	1.00	6.6
CaO	2.14	1.00	9.6
Al_2O_3	2.36	.94	12.8
Fe_2O_3	2.21	.93	21.5
Fe_3O_4	2.15	.90	35.1

Free Energies of the Oxides.—Lewis, Gibson and Latimer[1] have calculated the entropies of the various elements at 298° K. Using their values in conjunction with our entropy results for the compounds, we have obtained the figures for ΔS_{298}, the entropy of formation of each oxide from its elements, which appear in Table VIII, Column 2.

We are now in a position to calculate ΔF_{298}, the free energy of formation of each oxide, by means of the fundamental thermodynamic equation,

$$\Delta F = \Delta H - T\Delta S,$$

where ΔH is the increase in heat content during the process of forming the compound from its elements and is numerically equal to the negative of the heat of formation. The values selected for ΔH_{298} in the case of each oxide appear in the third column of the following table. For MgO and Al_2O_3 we have employed a mean between the results of Berthelot[1] and those of Moose and Parr.[2] The figure for CaO is that obtained by Guntz and Benoit[3] in their recent investigation. For the two oxides of iron we have used the heats of formation as calculated by Tigerschioeld[4].

---

[1] Lewis, Gibson and Latimer: J. Am. Chem. Soc., 44, 1008 (1922).

The resulting free energies appear in the last column. In their present form they are probably accurate to 1%. In the future, however, the accuracy of these ΔF values can be considerably increased by revision, as more reliable data for ΔH become available.

TABLE VIII

Thermal Data per Formula Weight

Substance	ΔS_{298} Entropy units	ΔH_{298} Cal.	ΔF_{298} Cal.
MgO	−25.7	−144,700	−137,000
CaO	−25.0	−152,800	−145,300
Al_2O_3	−72.8	−378,000	−356,300
Fe_2O_3	−63.9	−197,500	−178,400
Fe_3O_4	−81.0	−271,000	−246,800

Summary

1. The heat capacities of magnesium oxide, calcium oxide, aluminum oxide, ferric oxide (two samples) and of magnetite have been measured over a wide range of temperatures. In the case of the last compound a heat-absorption region at 113°-117° K. has also been observed.

2. The entropies and free energies of the several compounds have been calculated.

Department of Chemistry,
Stanford University,
September 1, 1925.

---

[1] Landolt-Börnstein-Roth-Scheele: "Tabellen" (1923).

[2] Moose and Parr: J. Am. Chem. Soc., **46**, 2660 (1924).

[3] Guntz and Benoit: Ann. Chim., **20**, 33 (1923).

[4] Tigerschioeld: Chem. Abstracts **19**, 1085 (1925).

THE EFFECT OF SOLVENTS ON THE ABSORPTION SPECTRUM OF A SIMPLE AZO DYE*

BY WALLACE R. BRODE

Before starting an extended study of the absorption spectra of a number of mon-azo dyes, a series of experiments was made to determine the effect of various solvents on the absorption spectrum of benzeneazophenol and precautions necessary in the determination of the absorption spectra of dyes of this type. The literature contains considerable theorizing and some practical data on the question of the effect of the solvent on the absorption band of dyes.[1] Kundt[2] said that the absorption band of dye is shifted towards the red end of the spectrum, i.e., to lower frequencies, with an increase in the refractive index of the solvent. This rather broad statement has since been known as Kundt's law. However, there have been nearly as many data reported in contradiction of it as in support of it.

It is certain that the refractive index of a compound is a function of its molecular constitution, and that in homologous series, the molecular refraction always increases with an increase in molecular weight. But it is not true that two isomeric substances such as methyl formate and acetic acid, or ethyl alcohol and di-methyl ether, have the same refractive index. Conversely, substances with the same refractive index do not necessarily have the same molecular constitution, and it follows that a dye dissolved in such solvents should not necessarily give the same molecular vibration. For example, benzyl alcohol and tetralin (tetrahydronaphthalene) have about the same refractive index, (1.540) which is rather high for organic solvents. Benzeneazophenol gives in benzyl alcohol a frequency of 845 f, 15 lower than in ethyl alcohol, while in tetralin the band is at a frequency of 875 f, some 15 higher than in ethyl alcohol, giving in all a difference of 30 in the center of the absorption bands in the two solvents used for the dye.

In general, little work has been done on the effect of the solvent on the absorption bands of azo dyes, and most of what has been done has been confined to the two solvents, water and alcohol. Only a few of the simple azo dyes which were to be studied in the course of this work, are soluble in water, hence it was necessary to use some organic solvent. The dye selected for the determination of the effect of the solvent on the absorption band, was benzeneazophenol. This dye was carefully prepared from purified intermediates, recrystalized repeatedly from alcohol, and dried in a vacuum oven at 60°

---

* This communication is an abstract of a portion of a thesis presented for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Presented before the Physical and Inorganic divisions of the American Chemical Society at Baltimore Md. April 8, 1924.

[1] Kayser: "Handbuch der Spektroscopie", 3, 80-89 (1905).

[2] Pogg. Ann. Jubelband, 615 (1874); Sitzungsber. Bayr. Akad. 7, 234 (1877); Ann. Physik, (3) 4, 34 (1878).

under reduced pressure. The dye gave a melting point of 152° corr. and analyzed 100% pure by titanous chloride titration.

In the neutral solution of benzeneazophenol in absolute ethyl alcohol there appears a very weak band near frequency 700, Fig. 1., so weak that it can scarcely be called a regular band, although the effect has been observed by a number of observers. This is followed by the principal band at a frequency 860 f, following which comes a region of fairly high transmission and then a third band at a frequency of 1280 f. The last or third band is at about the limit of the spectrophotometric measurements obtainable in the ultra-violet. It will be noticed that the third band is an exact multiple of the second band, the third band being 3/2 of the second band, or the bands correspond to the second and third members of a series of which the first would be 430 f or the fundamental frequency and the difference between each band being 430 f on the frequency scale. In an aqueous alkaline solution there appear bands at 710 and 770 f and a third weaker one at 1150 f, which is again 3/2 of the second band; this time, however, the first band is slightly greater in intensity than the second band. In alkaline alcoholic solution there appear bands at 660 and 735 f and a weaker band at 1125 f which is 3/2 of the second band. This time the first band is somewhat weaker than the second band. In concentrated HCl a third set of bands occurs with frequencies of 630, 940 and 1200 f.

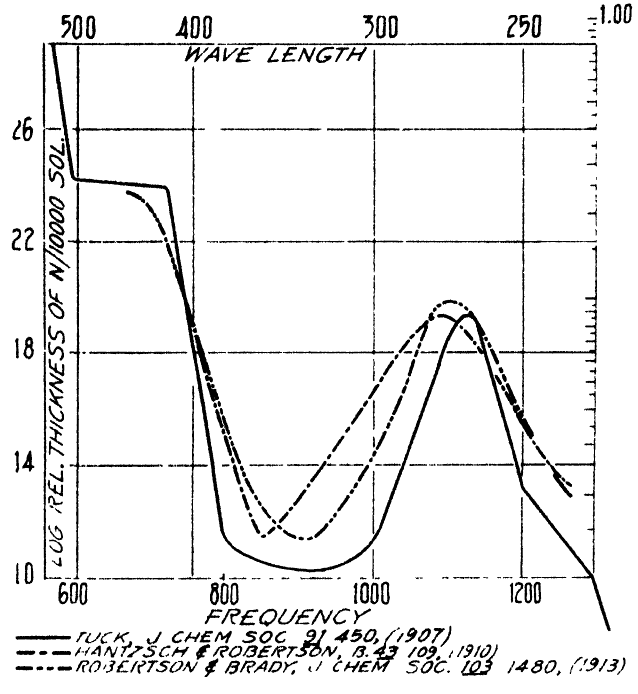


Fig. 1
Absorption Spectra of Benzeneazophenol in Alcohol.

We are primarily interested in the neutral series of bands, however, and will limit this discussion to that set of bands. The first band, if it may be called such, Fig. 1, is very much weaker than any of the others, so much so that its height and center of vibration can not be accurately determined in solutions where the other bands are at a height that can be accurately measured. We will therefore disregard the first band and confine our attention to the second or principal absorption band of the dye (860 f.). One of the principal reasons for choosing this particular dye was the fact that its main absorption band, although so far out in the ultra-violet as to prohibit the use of some solvents, owing to their absorption, is very sharp and apparently consists of only one band, in contrast to the apparent double band formation present in the more complex azo dyes. No conclusions can be drawn as to the effect of solvents on the third band owing to the position it occupies in the extreme ultra-violet and the fact that nearly all the solvents used absorbed in that region so as to make observation impossible.

Method

The Hilger sector photometer method with quartz spectograph was used in the determination of the ultra-violet spectral transmission of these solutions. The radiant energy source was an arc between tungsten electrodes under distilled water, which gave a continuous spectrum from the visible throughout the ultra-violet as far as the plates recorded. A high voltage high frequency current was used for this arc, the source of it being a large Tesla coil. The apparatus and the method of manipulation are described in detail in Scientific Paper 440 of the Bureau of Standards.

The extinction coefficient[1] which is plotted as the logarithm of the transmittancy, is shown on the accompanying graphs as a negative value and as such is plotted downwards on the ordinate. As a result the "peak" or point of maximum absorption of the band is really the lowest point rather than the highest. In this paper this point of maximum absorption will be referred to as the peak. The transmittancy is defined as the ratio of the energy passing through the cell containing the solvent and the dye, to that which passes through the cell containing only the solvent, (I/I′).

The transmittancy is thus given as

$$T = 10^{bck}$$

$$\text{or} - \log T \; 1/bc = k,$$

where *b* is the thickness in cm., *c* the concentration in cg. per liter, and *k* the extinction coefficient. In this paper the cell thickness was always 1 cm., while the concentration was maintained at 1.44 cg. per liter, and the extinction coefficient refers to the absorption of a solution containing 1.44 cg. per liter rather than 1. cg. per liter.

---

[1] Bureau of Standards Scientific Paper, No. 440; J. Opt. Soc. America, 10, 169 (1925).

The frequencies are plotted as *true* frequencies which is equivalent to 3×10^5 times the reciprocal of the wave length, rather than 10^5 times the reciprocal of the wave length as has often been done. The unit of frequency is defined as vibrations divided by (seconds $\times 10^{12}$) = f, the fresnel.

The exposure ranged in general from about three minutes at the maximum to 10 seconds at 100% transmittancy. Each exposure resulted in two spectra, parallel and in contact with each other, the lower one representing the energy passing through the solvent containing the dye, this beam of energy being unimpeded by any absorbing agent other than the dye in the solvent. The upper band represents the energy passing through the clear solvent. In the path of this latter beam there is a rotating sector which may be set at various transmittancies. These transmittancy values are so chosen as to be equivalent to units of .05 on the log of the transmittancy scale, i.e., actual transmittances such as 100, 89.4, 79.5, 71.0, 63.1, 56.4, etc. which are equivalent to log transmittancy values of .00, .05, .10, .15, .20, .25, etc. This required from 35 to 40 sets of exposures for each solvent. These values were checked again at the maximum and at 100% transmission by some 10 more exposures on a newly made solvent solution so as to verify the previous measurements. In Fig. 2 are given curves of benzeneazophenol by various observers which have been recalculated on the basis of percentage of thickness of a solution of constant transmission and to true frequencies of vibration.

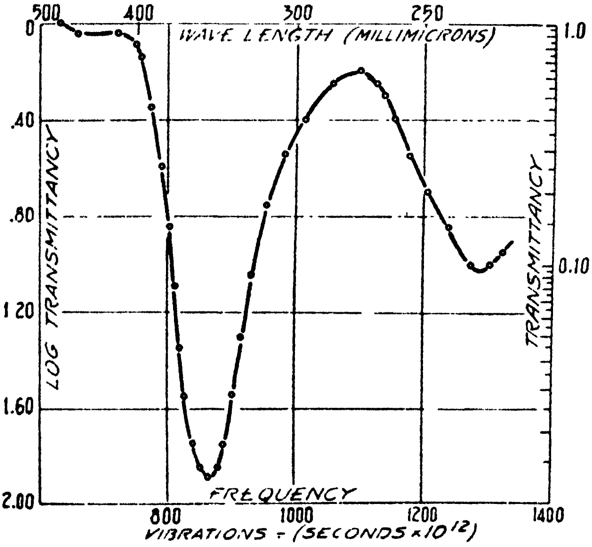


FIG. 2

Benzeneazophenol in Absolute Alcohol. Conc. = 1.44 cg per liter, thickness = 1 cm.

Solvents and Preparation of Solutions

The solvents which are listed below were used for these observations. All but carbon disulfide permitted the determination of the absorption maxi-

TABLE I

Solvents and their refractive indices and dielectric constants

No.	Solvent	MW	D	M	n	n_c	e	e_c	Quality
1	Methyl Alcohol	32.04	.7914	8.34*	1.331	—	31.2	2.40	Absolute
2	Ethyl Alcohol	46.06	.7894	12.9*	1.362	1.125	27.5	2.36	Absolute
3	iso Propyl Alcohol	60.08	.7887	17.5*	1.385	1.131	22.4	2.27	C. P.
4	n Butyl Alcohol	74.10	.8099	22.2*	1.399	—	19.2	—	Good
5	act. Amyl Alcohol	88.11	.816	26.8*	1.409	—	16.0	—	C. P.
6	Benzyl Alcohol	108.1	1.0415	32.5*	1.540	—	14.0	—	C. P.
7	Ethyl Acetate	88.1	.900	17.7*	1.374	1.128	6.1	1.82	C. P.
8	Butyl Acetate	116.1	.882	31.6*	—	—	5.0	1.70	Good
9	Amyl Acetate	130.1	.866	36.2*	1.406	—	4.8	—	C. P.
10	Ethyl Formate	74.1	.9064	17.7*	1.360	1.127	9.1	2.04	Very Good
11	Ethyl Propionate	102.1	.891	26.9*	—	—	5.6	—	Very Good
12	Ethyl Oxalate	146.1	1.081	33.2*	1.410	—	8.0	—	C. P.
13	Ethyl Benzoate	150.1	1.051	41.8*	—	—	6.0	—	Very Good
14	Ethyl Ether	74.1	.719	22.3*	1.355	1.113	4.3	1.71	C. P.
15	Acetone	58.1	.792	16.1*	1.360	—	21.5	—	Redistilled
16	Ethyl Methyl Ketone	72.1	.810	20.7*	1.380	—	18.0	—	C. P.
17	Formic Acid	46.0	1.190	8.3*	1.372	—	62.0	—	C. P. (85%)
18	Acetic Acid	60.0	1.051	12.9*	1.347	1.127	9.7	1.99	C. P. (Glacial)
19	Chloroform	119.4	1.499	21.4*	1.449	—	5.1	—	U. S. P. (1% Alcohol)
20	Carbon Tetrachloride	153.8	1.584	26.3*	1.463	1.165	2.24	1.34	C. P.
21	Carbon Disulphide	76.1	1.256	—	1.631	—	—	—	C. P.
22	Glycerol	92.1	1.206	20.6*	1.472	—	56.?	—	C. P.
23	Ligroin	C-6	.660	29.9*	1.395	1.133	1.90	1.26	Redistilled
24	Gasoline	C-9	.680	48.3*	1.400	1.132	1.92	1.26	Redistilled
25	Petrolatum	C-15	—	76.1*	1.403	—	1.84	—	Medicinal
26	Benzene	78.1	.879	26.3*	1.501	1.174	2.28	1.35	C. P. (Thiophene Free)
27	Toluene	92.1	.865	30.9*	1.498	—	2.37	—	C. P.
28	Xylene	106.1	.864	35.5*	1.498	—	2.35	—	C. P.
29	Tetralin	132.1	.974	—	1.540	—	—	—	Redistilled
30	Pyridine	79.1	.990	—	1.509	—	12.4	—	C. P.

MW—Molecular weight, D—density, M—molecular refraction, n—refractive index. n_c—refractive index at critical temperature[1], e—dielectric constant, e_c—dielectric constant at critical temperature[2], *—calculated value, not observed.

---

[1] Herz: Z. physik. Chem. 98, 175 (1922).

[2] Herz: Z. physik. Chem. 103, 269 (1922).

mum of the dye. The solvents used were thought to be of high purity, with the possible exceptions of butyl alcohol and butyl acetate, which showed indications of impurities in their ultra-violet spectrum. A number of the solvents used were redistilled in the laboratory. It is entirely possible that the carbon disulfide used although of c.p. grade contained a small amount of free sulfur, which would have increased the absorption of the solution.

The black portion in Fig. 3 indicates the region where total absorption takes place as determined through a 1 centimeter cell on exposure of not over

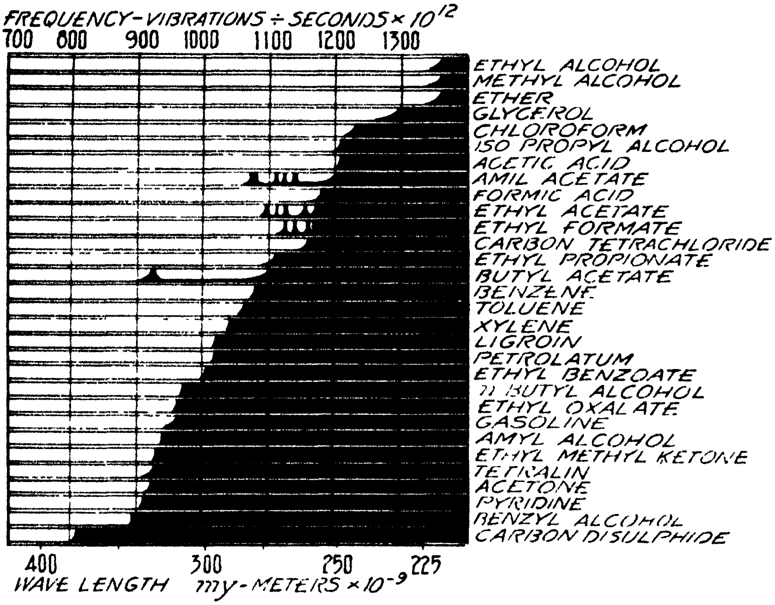


Fig. 3

Absorption of solvents used for 1 cm. thickness. Slope of start of band indicates whether the absorption is sharp or gradual.

3 minutes nor less than 2 minutes. The slope of the start of the absorption strip indicates whether the absorption commences abruptly or gradually, as determined by a series of exposures varying from 10 seconds to more than two minutes. The accuracy of the determination of the limit of transmission of these solvents can better be determined by direct examination of the plates (not reproduced in this paper). The esters were the only solvents which showed satellite bands. In all probability the other solvents would have shown bands if the cell thickness had been reduced, as it requires a relatively weak band to exhibit anything but total absorption in a thickness of 1 cm.

The graph of the absorption limits of these solvents gives a series of solvents with gradual absorptions from 1350 to 800 f and in practically all cases, except where indicated, the absorption is very sharp so that they may be used conveniently as radiant energy filters. The limit of the spectrograph used was about frequency 1360 to 1380 so that values in the neighborhood of this limit do not have as high an accuracy as those of lower frequencies.

By experiment it was found that a concentration of 1.44 centigrams per liter would give a curve with a maximum extinction coefficient of about 1.80, which was a convenient value to work with. The solutions used were made up in two ways, first, by dissolving .1900 g. of the dye in 500 cc, pipetting off 40 cc of this and making it up to 200, and pipetting off 40 cc of this solution and making it up to 200 cc. This procedure was followed when the dye dissolved with difficulty or the solvent was easily obtainable in large quantities. The second method was to dissolve .1440 g. in 100 cc of solvent, pipette off 10 cc of this and make up to 100 cc and pipette off 10 cc of this solution and make it up to 100 cc. The solutions were made up at 20° and samples of the clear solvent removed at the same time.

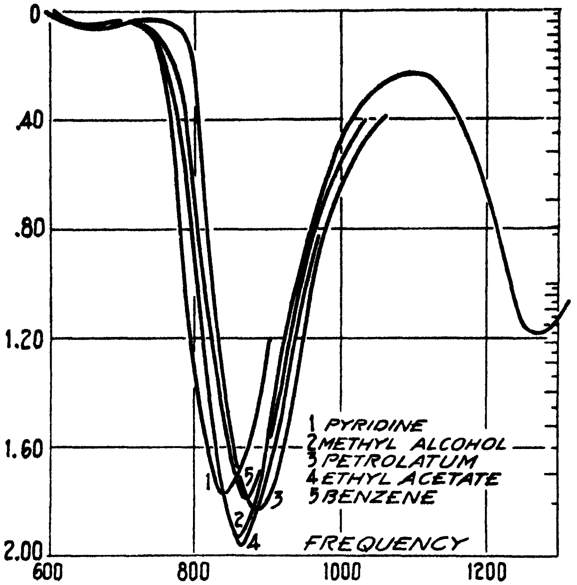


Fig. 4

Absorption Spectra of Benzeneazophenol in Pyridine (1), Methyl Alcohol (2), Petrolatum (3), Ethyl Acetate (4), Benzene (5).

In the case of glycerol, considerable error was possible, owing to the viscosity of the solvent, so that it was necessary to wash the pipette out several times with the diluting solvent so as to insure as complete a draining of the pipette as possible. In the case of the other solutions the pipettes were simply allowed to drain. The dye dissolved with difficulty in the petroleum solvents and glycerol, it dissolved quite readily in the other solvents. The temperature of the cells when the observations were made was between 21° and 23°.

Results

The results obtained are best illustrated graphically. In Fig. 4 are given curves for the dye in methyl alcohol, pyridine, benzene, petrolatum and ether. In the following table are given values for the extinction coefficient and frequency at the peak, for all the solvents used.

TABLE II

Frequency and height of the absorption band of benzeneazophenol in the solvents used.

	Solvent	F.	Extinction Coefficient
1	Methyl Alcohol	862	1.90
2	Ethyl Alcohol	860	1.90
3	iso Propyl Alcohol	859	1.88
4	n Butyl Alcohol	854	1.91
5	act. Amyl Alcohol	853	1.92
6	Benzyl Alcohol	859	1.90
7	Ethyl Acetate	862	1.98
8	Butyl Acetate	861	1.90
9	Amyl Acetate	865	1.95
10	Ethyl Formate	866	1.98
11	Ethyl Propionate	864	1.86
12	Ethyl Oxalate	866	1.89
13	Ethyl Benzoate	855	1.84
14	Ethyl Ether	861	1 95
15	Acetone	865	2.00
16	Ethyl Methyl Ketone	860	1.90
17	Formic Acid	863	1.15*
18	Acetic Acid	870	1.85
19	Chloroform	871	1.85
20	Carbon Tetrachloride	880	1.80
21	Carbon Disulfide	—	——
22	Glycerol	856	1.60
23	Ligroin	885	1.92
24	Gasoline	884	1.92
25	Petrolatum	883	1.84
26	Benzene	871	1.80
27	Toluene	868	1.70
28	Xylene	871	1.74
29	Tetralin	865	1.74
30	Pyridine	840	1.64

*See Fig. 5.

From the above data it can be seen that as far as the height of the band is concerned, with a few exceptions, the band is lower in non-polar solvents. The measurements on the height of the band, however, are not as accurate as the frequency measurements and allowance must be made for instrumental errors involved in the photographing and in the reading of the plates after photographing. This is in part due to the fact that the band is flat for a very short distance at the maximum, or rather gives the appearance of such, and in such cases the greater accuracy is obtained by changing the transmission valves gradually, a process which is impossible photographically. The error involved in the determination of the frequency does not amount to more than ± 2 in most of the cases observed except where the absorption of the solvent was near enough to the peak of the band to decrease the intensity.

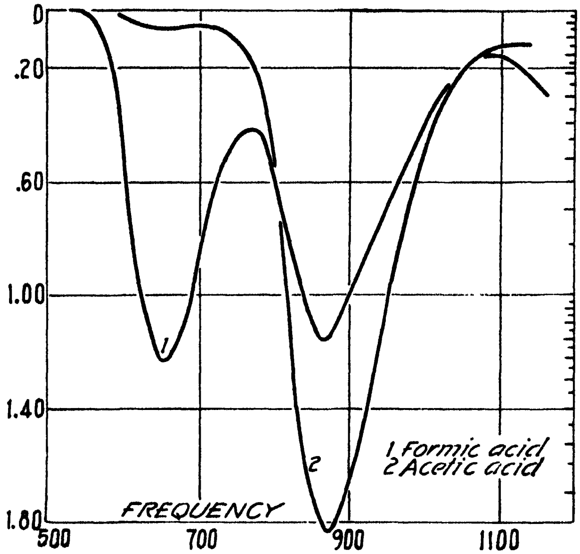


FIG. 5

Absorption Spectra of Benzeneazophenol in 85% Formic Acid (1) and Glacial Acetic (2). Note acid band which is produced by formic acid.

The general shape of the band is the same for all of the solvents, indicating a general shift of the entire band rather than the increasing of certain frequency amplitudes within the band structure with the decreasing of others, as it is highly improbable that if the latter were the case the change would be exactly analogous in all cases so as to give the same shaped band but with a different vibrational center.

From Fig. 6 it is evident that there is very little if any relation between the refractive indices of the various solvents used and the frequency of the absorption maximum, although in the case of certain homologous series such as the alcohols there seems to be a general shift with an increasing molecular weight. It is also to be noticed that similar solvents in general group together although the order in which they arrange themselves is not consistent with the increase of their refractive indices. Although there are a large number of exceptions, in fact too many to permit such a conclusion, it appears that the average shift is towards higher frequencies with increasing refractive indices, an effect exactly opposite to Kundt's law.

In Fig. 6 are compared the refractive indices and frequencies of the peak of the band in different solvents which are numbered as in Table I and II. In like manner the effect of the dielectric constant which is also considered a molecular property of the solvent, appears to have very little effect, Fig. 7, but here again, it may be pointed out that in homologous series there may be some relation. This relation in regard to homologous series may and probably is due to some other effect than a change in the dielectric constant or refractive index, although this effect and the force which changes the dielectric constant and refractive index are probably fundamentally related. As would be expected, similar substances such as xylene and tetrahydronaphthalene (tetralin) give similar frequencies of vibration and also closely related dielectric constants and refractive indices.

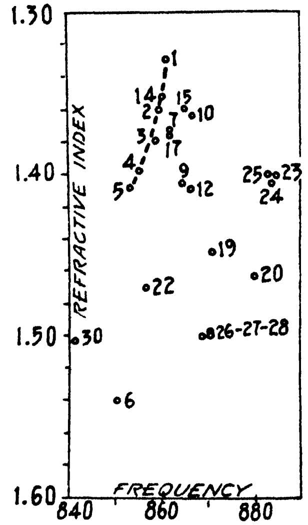


FIG. 6

Relation between the refractive index at 20° and the absorption frequencies. The numbers refer to the solvent numbers in Table II.

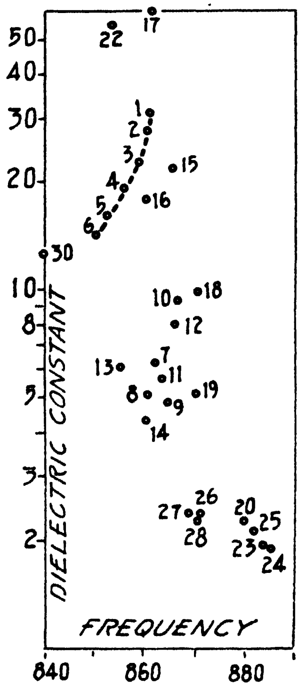


FIG. 7

Relation between dielectric constants at 20° and absorption frequencies.

By plotting the frequency values of the absorption band of the dye in some of the various solvents against their refractive indices or dielectric constants figured over to the theoretical value at their critical temperatures a somewhat better agreement is obtained and some of the discrepancies which existed before, as in the case of the saturated hydrocarbons and the aromatic hydrocarbons are corrected. There are still too many exceptions and deviations to draw any conclusions, Figs. 8-9. The values have also been plotted for the dielectric constants at their boiling points with about the same agreement, or disagreement, depending upon the angle from which it is viewed, Fig. 10. The objection may be raised, and it is quite legitimate, that the observations were not made at these temperatures and that comparison is being made between two unrelated sets of figures. It may be pointed out, however, that the shift of the absorption band with temperature is slight, especially with azo dyes[1] whereas the changes in the refractive indices and dielectric constants with change in temperature are large and the values widely varied, but that at the critical temperature or boiling point they fall into a more regular series with a more uniform change.

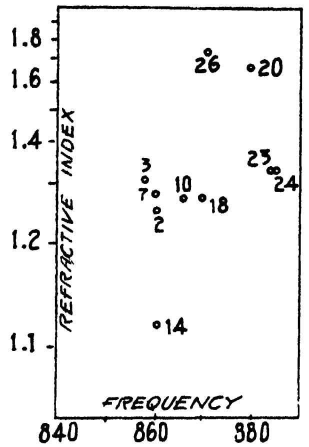


Fig. 8

Relation between refractive indices at the critical temperature and absorption frequencies of the solvent.

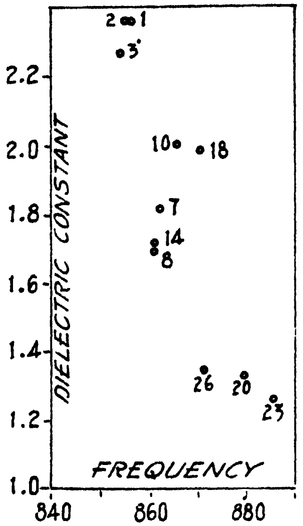


Fig. 9

Relation between the dielectric constants at the critical temperature and the absorption frequencies.

Mixed Solvents

In determining the effect of a solvent on the absorption maximum of a dye it was quite essential to determine the effect of mixed solvents, or the effect of an impurity on the shift in the absorption band. In these experiments, solutions of benzene and alcohol, carbon tetrachloride and alcohol, ligroin and alcohol, water and alcohol, and ligroin and benzene were used. The first two

---

[1] Bureau of Standards Sci. Papers, No. 440; Kayser; "Handbuch der Spektroscopie", 3, 92.

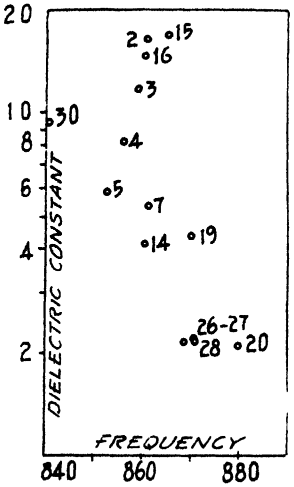


FIG. 10

Relation between dielectric constants at the boiling point and absorption frequencies.

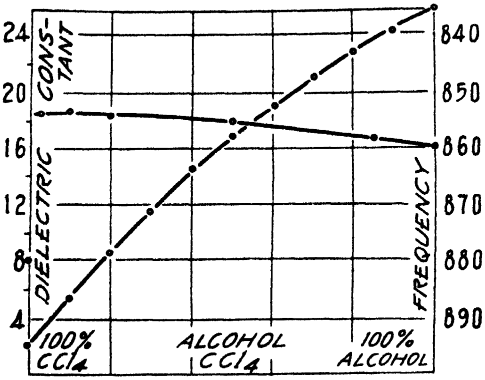


FIG. 11

Effect of mixtures of alcohol and carbon tetrachloride on the dielectric constant and absorption frequency.[1] Dotted line = frequency.

[1] Givan and Patrick: J. Am. Chem. Soc., **45**, 2799 (1923).

of these were of special interest as data were available on the dielectric constants and refractive indices of these mixtures. From these data a careful check could be obtained on the relation between the absorption shift and the refractive indices and dielectric constants. The results are indicated in Figs. 11-13. The effect, although one which might be predicted, is far from being a function of either of these two physical properties. As small an amount of alcohol as 1% was sufficient to shift the band to the alcohol band in both benzene and carbon tetrachloride. The shift is quite apparent and would

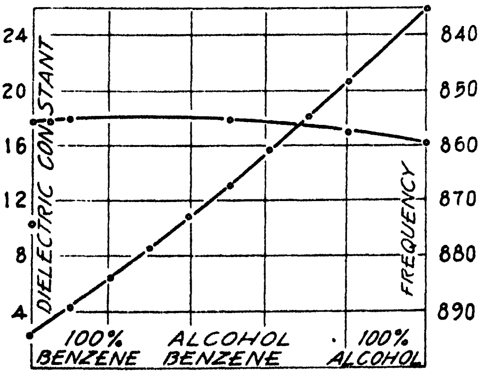


FIG. 12

Effect of mixtures of alcohol and benzene on the dielectric constant and absorption frequency.[2] Dotted line = frequency.

[2] King and Patrick: J. Am. Chem. Soc. **41**, 1143 (1921).

undoubtedly have taken place for much smaller concentrations of alcohol, the 1% solution being the lowest percentage tried. It is apparent that the more polar the solvent the greater tendency it has to shift the band to its own vibratory frequency giving the effect of the dye being entirely dissolved in the solvent, and this solution being suspended in the other solvent. In the case of ligroin and benzene the effect appeared to be a gradual change as compared with the sharp change due to alcohol. In both the benzene and the carbon tetrachloride mixtures the band seemed to shift to a point somewhat beyond the ordinary frequency of alcohol (855) and then on increasing the percentage of alcohol it gradually returned to 860. The same effect was noticed on dilution of the alcohol solution with water. The band was gradually reduced in frequency with an increase in the water percentage to about the same values, indicating possibly that the effect is merely one of dilution. The dye being insoluble in water, there is no shifted band in this case, the main band being simply reduced in intensity. This reduction does not take place until the percentage of alcohol becomes very small. This effect accounts to some extent for some of the wide variations in the shifting of the band, as in the case of the chloroform which was known to contain a small amount of alcohol and in which the band was not shifted to anywhere near the extent to which it was shifted in carbon tetrachloride.

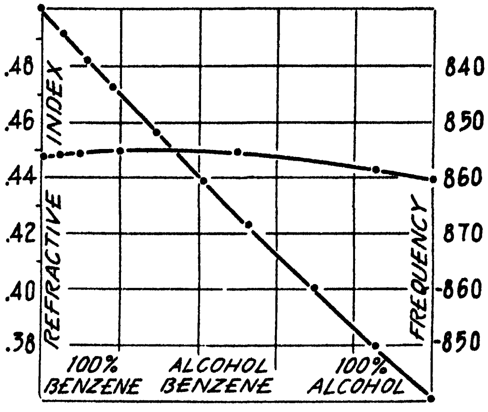


FIG. 13

Effect of mixtures of alcohol and benzene on the refractive index and absorption frequency. Dotted line = frequency.

Summary

1. The absorption limits of some 30 organic solvents have been determined and their region of total absorption has been observed throughout the ultra-violet to a frequency of 1360 for a thickness of 1 cm.

2. The absorption spectrum of benzeneazophenol has been observed in these solvents.

a. From these data it appears that for this simple azo dye, and in all probability for other simple azo dyes, Kundt's law does not hold.

b. There appears to be no definite relation between the refractive indices or the dielectric constants of these solutions and the frequency of the absorption band of the dye dissolved in them.

3. In mixtures the dye appears to give the absorption frequency for the most polar solvent, even if this solvent is present in a very low percentage and there is a slight dilution effect in such cases.

4. The height of the band appears to be greater for polar solvents than for non-polar solvents.

SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS
VI. SOLUBILITY OF THE NITROANILINES IN VARIOUS LIQUIDS

BY ARMAND R. COLLETT AND JOHN JOHNSTON*

This investigation of the solubility of the three nitroanilines in a series of liquids was undertaken with two main objects in view. The first was to discover, if possible, whether some particular solvent would be specially advantageous in the separation of a mixture of such isomers, or in the purification by crystallization of any one of them. The second was to learn more as to the solubility relations of such closely related substances as the *ortho*, *meta* and *para* isomers C_6H_4XY. It was hoped moreover that any conclusions which could be drawn from the behavior of one series could be applied—at least as a first approximation—to other series which are not too dissimilar.

The substances chosen were the nitroanilines, which are readily obtainable in a pure state and are convenient to work with. Although these compounds are important dye intermediates, little reliable information on their solubility is available; for, with the exception of the work of Bogojavlenski et al.[1] on their solubility in benzene, nitrobenzene, and dibromoacetylene, and the more recent work of Sidgwick and Rubie[2] in benzene and in water, only questionable data at 20° and 25° are available. The solvents investigated were selected as typical substances in common use as solvents.

Materials

In purifying the nitroanilines by recrystallization we found the process to be more effective with two solvents used separately than with a single solvent; it is questionable however, as we shall see, in how far the use of a second solvent is in general beneficial in the separation of one isomer from the other.

Ortho-Nitroaniline was crystallized from 95% alcohol and then repeatedly from hot water, from which it came out in fine orange-colored needles. The melting temperature as determined from the flat on the time-temperature curve[3] is 69.3°, although by the ordinary capillary tube method it appears to be 72°.

Meta-Nitroaniline was crystallized twice from alcohol and then from water; this yielded lemon-yellow blade-like crystals, the melting temperature of which is 111.8°.

Para-Nitroaniline, crystallized several times from water, yielded, on solution in hot alcohol, a reddish residue; so it was recrystallized from alcohol and subsequently from water. The final product consisted of light yellow needles the melting temperature of which is 147.5°.

---

*From the dissertation presented to the Graduate School of Yale University, in June, 1923, in candidacy for the degree of Doctor of Philosophy.

[1] Bogojavlenski, Bogoliubov and Vinogradov: through Chem. Abs. **1**, 2875 (1907).

[2] Sidgwick and Rubie: J. Chem. Soc., **119**, 1013 (1921).

[3] Cf. Kohman: J. Phys. Chem., **29**, 1048 (1925).

Water: all the distilled water used was boiled to expel dissolved air.

Alcohol: 95% alcohol was refluxed with lime, distilled, dried with sodium, and redistilled twice; the major fraction boiled at 78.4° and 762 mm.

Benzene: Pre-war thiophene-free benzene was dried over sodium and distilled; redistillation yielded a major fraction boiling at 80.3-80.4° and 762 mm.[1]

Chloroform (C. P.) was dried for several days over calcium chloride and then distilled; it boiled at 61.2-61.4° and 768 mm.

Carbon tetrachloride (C. P.) was treated similarly; it boiled at 76.5-76.55° and 765 mm.

Ether (U. S. P.) was washed several times with sodium carbonate solution, subsequently with water until the aqueous layer proved to be neutral. After being dried for a week over calcium chloride, it was distilled twice; the product boiled at 34.5-34.8° and 760 mm.

Ethyl acetate (U. S. P.) was treated similarly; it boiled at 77.0-77.3° and 760 mm.

Acetone (C. P.) was dried over calcium chloride and twice distilled; the fraction used boiled at 56.1-56.2° and 756 mm.

Every effort was made to prevent moisture from reaching the solvents; the distillation apparatus was thoroughly dried, and the solvents were preserved in flasks stoppered with a calcium chloride tube.

Method

Most of our determinations have been made by a slight modification of the synthetic method which has been used by a number of previous investigators[2]; a few were made by analysis of the solution saturated at a fixed temperature, as a check on the accuracy of the synthetic method. The essence of this method is to ascertain the temperature at which the last crystal just disappears, when a known mixture of solute and solvent is slowly heated. The chief objections to this procedure, as usually carried out, are that the observed saturation temperature may be in error because the rate of change of temperature is not slow enough to insure the attainment of equilibrium, of composition or of temperature, and that the composition of the solution may change owing to volatilization of the components. The procedure finally adopted, after a large number of preliminary experiments (not detailed here) is substantially free from these objections, and yields results which compare favorably with those obtained by analysis of a solution in contact with crystals of a definite temperature; it is as follows. Into a small bulb, of 2-4 cc. capacity, blown on a tube about 6 mm. diameter, was introduced a known weight of the substance; the tube was drawn down to capillary size at a distance of 3-4 cm. from the bulb, an appropriate quantity of solvent introduced, the tube sealed off and weighed so as to secure the weight of the solvent. The tubes were not completely filled, a space, usually about 1 cc., being left to permit of stirring, which was accomplished by attaching the tube horizontally to a heavy wire which had been soldered to the (vertical) hammer of an ordinary electric bell; this proved to be an effective method of agitation, and was used throughout the series of observations. The tube was now surrounded by a three-liter beaker containing either water (up to 80°) or paraffin (beyond 80°) which was kept thoroughly stirred by a stream of air; and a calibrated thermometer, graduated in tenths, was immersed so that its bulb was close to the tube, a second thermometer being used to enable the proper stem correction to be made. The flame was adjusted so that the rate of heating of the bath was about 0.1° per minute, and the temperature noted at which the last crystal disappeared; the bath was now allowed to cool slowly until about half the solute had crystallized, whereupon it was again raised in temperature and maintained for half an hour at about 1° below that first recorded. Finally the bath temperature was raised at about 0.05° per minute, and the temperature at which the last crystal now disappeared was taken to correspond to saturation for the particular mixture weighed into the tube. Determinations made in this way check within about 0.2°; whereas, if one may judge from the data, the corresponding divergence in many of the previous results obtained by this general mode of experiment, has been 1° or even more. A correction (which in all cases was small) was made for the change in composition caused by the presence of some of the solvent in the vapor space; it was computed from the vapor pressure of the pure solvent, and its mol fraction in the solution on the basis that Raoult's law holds. A similar calculation showed that the corresponding correction for the nitroanilines is negligible.

---

[1] Richards and Barry give 80.2° at 760 mm: J. Am. Chem. Soc., **37**, 996 (1915).

[2] Alexeiev: Ann. Physik, **28**, 327 (1886); Schröder: Z. physik. Chem., **11**, 449 (1893); Bogojavlenski, Bogoliubov and Vinogradov: through Chem. Abs. **1**, 2874 (1907); Sidgwick et al: J. Chem. Soc., **107**, 1202 (1915); **119**, 979, 1001, 1013 (1921); **121**, 1844, 1853, 2256, 2263, 2536 (1922); **123**, 2813, 2819, (1923); Kendall et al: J. Am. Chem. Soc. **43**, 979 (1921); **45**, 958 (1923); Carrick: J. Phys. Chem., **25**, 648 (1921).

In the analytical determinations, solvent with excess of solute was placed in glass-stoppered bottles with gum covers, or in sealed tubes, which were rotated in a thermostat. When equilibrium had been attained, the solid was allowed to sttle, and filtered samples of the solution were weighed and analyzed. A search of the literature for a method of analysis for nitroaniline revealed only one which appeared satisfactory[1] namely, that of Knecht and Hibbert[2], who titrate with titanous chloride in absence of oxygen. Their procedure however had to be modified somewhat to give the accuracy desired. The solution of titanous chloride, $TiCl_3$, used was approximately 0.2 normal; it was kept under an atmosphere of hydrogen, as described by Knecht and Hibbert. Methylene blue, prepared by adding 0.5 grams of methylene blue to 500 cc. of water, shaking and filtering, was used as indicator; it was reduced to the colorless condition with $TiCl_3$ and kept in an atmosphere of carbon dioxide. With

[1] As has been shown by Carnelley and Thomson, (J. Chem. Soc., **53**, 782 (1887)) and from our observations, the amount of nitroaniline in a solution cannot be estimated by evaporating the solvent owing to the high volatility of the solute; even at 40° appreciable amounts of nitroaniline are volatilized. Yet as late as 1904 Farmer and Warth (J. Chem. Soc., **85**, 1713 (1904)) used this inaccurate method. The colorimetric method used by Carnelley and Thomson was not adopted in this case because of the inaccuracy, as suggested by the authors themselves, resulting from the color change of the solutions on exposure to light.

[2] Knecht and Hibbert: Ber., **40**, 3819 (1907); **36**, 1549 (1903); q.v.

these solutions the experimental error in analysis was easily reduced to 0.5% when the samples titrated were from 0.05 to 0.5 grams. The presence of the solvents employed in this investigation was found to have no effect upon the results; Knecht and Hibbert give a correction for the effect of the alcohol, but this difference probably results from the fact that they did not boil the solution and consequently did not expel the dissolved air before they added the titanous chloride.

TABLE I

Mean Experimental Results on the Solubility of the Nitroanilines in Various Solvents, as determined analytically.

Solvent	Temp. C. t	Solubility g. per 100 g. solvent	 mols per 100 mols solution C
	Ortho		
H_2O	25.0	0.1212	0.158
	40.1	0.2423	0.315
C_6H_6	25.0	20.80	10.52
C_2H_5OH (abs.)	25.0	27.87	8.47
$CHCl_3$	0.0	11.17	8.81
	Meta		
H_2O	25.0	0.0910	0.119
	40.1	0.1785	0.232
C_6H_6	25 0	2.718	1.53
	40.1	5 137	2.82
C_2H_5OH (abs.)	0 0	4.035	1.33
	25.0	7.778	2.53
C_2H_5OH (95%)	25.0	7.155	——
$CHCl_3$	0.0	1 358	1.16
	25.0	3.216	2.60
	40.1	6.102	5.01
	Para		
H_2O	25.0	0.0568	0.074
	40.1	0.1157	0.151
C_6H_6	25.0	0.5794	0.325
	40.1	1.040	0.555
C_2H_5OH (abs.)	0.0	3.382	1.110
	25.0	6.048	1.978
	40.1	8.234	2.674
C_2H_5OH (95%)	25.0	5.674	——
$CHCl_3$	0.0	0.4331	0.373
	25.0	0.9290	0.797
	40.1	1.559	1.330

The results of the determinations by the analytical method are presented in Table I, each datum being the mean of from three to five concordant measurements made by approaching the equilibrium both from under- and from over-saturation.

The direct experimental saturation temperatures (t) secured by use of the synthetic method are presented in Table II, in terms of mol percentage[1] (C) of solute (corrected only for the amount of solvent in the vapor space). For convenience of reference, we have included the results of Sidgwick and Rubie, recalculated in terms of mol-percentage. Solutions of *meta*-nitroaniline and carbon tetrachloride, containing from 60-85 mol percent of the former, break up into two liquid layers, with some decomposition. The same thing happens with *para*-nitroaniline in carbon tetrachloride, even at concentrations as low as 45 mol per cent; consequently work on this system was abandoned. The results for the system *para*-nitroaniline-ether are less accurate than for the other solvents, by reason again of a partial decomposition, as evidenced by a charring of the solute.

TABLE II

Mean Experimental Results on the Solubility of the Nitroanilines in Various Solvents, as determined by the Synthetic Method.

Ortho-Nitroaniline

mol percent C	temp. t	mol percent C	temp. t	mol percent C	temp. t
Acetone		Ethyl Acetate		Chloroform	
46.75	32.3	40.43	32.3	26.30	28.2
50.21	35.8	52.74	44.0	33.29	34.0
62.67	47.8	70.41	55.6	43.82	41.2
75.24	57.4	84.18	63.6	57.17	48.6
80.37	60.8			78.07	60.4
				88.81	65.8

Ethyl Alcohol (abs.)		Ether	
16.14	37.7	21.11	29.5
31.56	47.1	25.30	35.1
47.49	51.7	42.84	47.1
64.30	56.7	57.98	52.9
66.61	57.6	78.86	62.3
79.27	62.0	80.60	62.8
88.70	65.9		

---

[1] The following molar weights were used: nitroaniline 138.1; benzene 78.05; chloroform 119.4; carbon tetrachloride 153.8; ethyl alcohol 46.05; acetone 58.05; ether 74.1; ethyl-acetate 88.06.

TABLE II (continued)

Carbon Tetrachloride

mol percent C	temp. t
5.26	41.3
13.24	47.8
21.29	50.0
31.19	51.6
46.44	53.1
58.32	55.5
74.06	60.2
84.68	64.2

Benzene

mol percent C	temp. t
14.56	31.2
32.78	42.4
46.18	47.9
58.49	52.6
76.71	60.3

Benzene (S & R)

mol percent C	temp. t
7.32	10.5
13.38	23.2
22.35	39.2
44.81	47.4
54.86	50.2
67.53	55.0
81.72	62.0
92.03	67.2
100.0	71.1

Meta-Nitroaniline

Acetone

mol percent C	temp. t
24.69	36.5
38.17	62.0
48.06	75.6
56.20	83.4
66.64	91.9
84.65	103.3

Ethyl Acetate

mol percent C	temp. t
19.82	38.9
22.84	48.9
36.91	71.3
49.61	83.0
61.74	91.5
81.49	103.1

Chloroform

mol percent C	temp. t
5.27	44.6
11.54	61.3
20.66	71.6
47.06	86.6
71.15	99.3
84.32	104.8

Ethyl Alcohol (abs.)

mol percent C	temp. t
5.64	50.2
11.40	65.9
23.25	78.5
36.80	85.0
45.57	88.7
61.32	94.7
69.76	98.4
82.52	104.6

Ether

mol percent C	temp. t
5.34	34.7
8.93	52.0
21.53	76.4
40.87	89.4
49.66	93.0
64.36	98.1
81.54	105.2

Carbon Tetrachloride

mol percent C	temp. t
5.19	87.3
13.84	94.7
17.53	95.8
19.29	95.9
33.76	97.2
45.41	98.8
55.90	99.6
86.72	100.0

Benzene

mol percent C	temp. t
13.56	70.4
24.21	79.5
36.57	85.4
48.99	90.5
56.85	92.7
77.04	102.1

Benzene (S & R)

mol percent C	temp. t
2.54	38.2
8.54	60.9
21.32	78.4
47.46	88.7
68.78	99.2
84.40	105.4
93.72	110.3
100.0	114.6

TABLE II (continued)

Para-Nitroaniline

mol percent C	temp. t	mol percent C	temp. t	mol percent C	temp. t
Acetone		Ethyl Acetate		Chloroform	
24.48	52.5	12.51	45.8	4.98	78.5
35.03	83.4	24.83	83.7	11.59	94.8
42.22	95.4	37.48	102.2	21.68	104.8
49.51	105.5	44.59	110.1	48.61	118.9
67.96	124.5	67.72	127.6	65.09	127.4
82.66	136.0	89.41	142.2	89.92	141.9
Ethyl Alcohol (abs.)		Ether			
2.45	34.8	3.688	66.6		
6.05	66.2	5.66	89.1		
16.96	92.0	9.53	104.6		
36.59	109.0	16.88	114.1		
44.19	113.7	20.53	117.1		
59.74	122.8	32.82	120.0		
74.45	132.3	51.77	126.6		
83.83	137.2	53.51	127.2		
		72.89	134.2		
		86.08	141.1		
		Benzene		Benzene (S & R)	
		4.61	90.9	1.84	70.0
		9.44	101.7	6.79	95.0
		22.49	113.3	16.04	108.6
		31.72	116.1	40.02	119.5
		40.62	119.8	60.16	122.5
		56.92	127.0	71.62	132.3
		83.61	139.5	94.42	143.7
				100.0	147.0

All of the data were plotted on a large scale, in terms of C vs. t[1], and the best curve drawn through, or very nearly through, the points. To draw these curves satisfactorily is not always easy, since many of them are initially concave, and at lower temperatures convex, to the C axis; and many show a very rapid change of slope at values of C around 10%. The only adjustments made, all of which were slight, were on the basis that the several curves should all converge to the melting temperatures of the solute, and should not cross one another in that region. The general form of the curves is evident from Fig. I, in which a number of them are reproduced. The graphs show that the results

---

[1] Plots of log C vs. 1/T, and of the data in terms of other variables, were tried and serve as a check upon the interpolation; but apart from this none of them in this case possessed any apparent advantage.

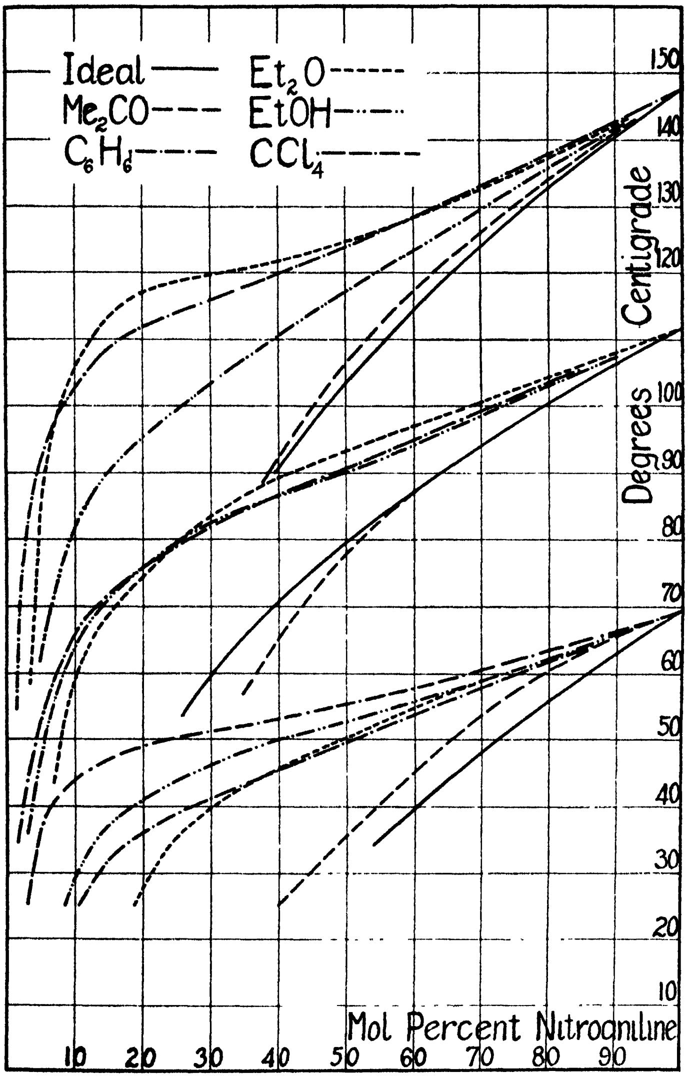


FIG. 1

secured by the two methods are in good accord. The only data with which ours may be compared are those on the solubility of each of the three isomers in benzene, as given by Bogojavlenski, Bogoliubov and Vinogradov[1] and by Sidgwick and Rubie[2]; both of these sets of data show small, and somewhat irregular, departures from our curve, the average difference however being less than 1°. For purposes of comparison, the data of the former authors on the solubilities in nitrobenzene and in dibromoacetylene were also plotted.

---

[1] Bogojavlenski, Bogoliubov and Vinogrsadov: through Chem. Abs. 1, 2874 (1907).

[2] Sidgwick and Rubie: J. Chem. Soc., 119, 1013 (1921).

Values of the solubility of each isomer in each solvent hitherto investigated, for a series of even values of *t*, obtained by interpolation on the large plots, are given in Table III[1]; it also includes the ideal values, as derived from thermal data, which are in fact found when the solvent is another of the nitroanilines[2].

Discussion of Results

Inspection of the solubility curves obtained shows that the corresponding curves for the three isomers are in general very similar, though there are also significant differences between them, these differences being evidently correlated with the melting temperature (presumably, also, with the heat of melting) of the isomer. For instance, the double curvature is barely appreciable in the case of the *ortho* (which has the lowest melting temperature), is somewhat greater with the *meta*, and most evident with the *para*.

At temperatures in the neighborhood of the melting temperature of each isomer, the sequence of the "solvents", arranged in order of decreasing solubility—or of decreasing effect in lowering the melting temperature—of the nitroaniline, is: ideal, acetone, ethyl acetate, (nitrobenzene), chloroform, (dibromo-acetylene), benzene, alcohol, ether, carbon tetrachloride. At temperatures farther from the melting temperature, however,—which is the region of practical importance—the sequence is not invariable because some of the curves cross; for instance, the pair for ether and benzene, intersect at about 40 mol per cent *ortho*, at 30 per cent *meta*, and at 6 per cent *para*. Again, over the great part of the range, the solubility of *ortho* in benzene is greater than in

TABLE III

Solubility of the Nitroanilines in Various Solvents, as interpolated at a Series of Temperatures, expressed in Terms of Mol-percentage.

Ortho (m.p. 69.3°)

Solvent			t		
	60	50	40	30	25
Ideal	85.9	72.5	60.6		
acetone	79.2	65.6	54.5	44.6	40.0
ethyl acetate	77.6	61.6	48.2	38.3	34.1
chloroform	77.3	60.0	42.0	28.4	23.0
benzene	75.8	51.6	27.6	13.6	10.5
ether	74.0	50.1	30.6	21.5	18.7
alcohol	74.0	40.3	18.7	10.4	8.5
CCl_4	73.9	21.1	4.6		
water			0.31		0.16
$C_6H_5NO_2$	76.0	56.4	39.8	29.0	24.8
C_2Br_2	76.0	56.4	39.8	29.0	24.8

---

[1] Some scattered data, mainly for 20°, may be found in Seidell: "Solubilities of Inorganic and Organic Compounds", 2nd Ed., p. 78-80.

[2] See Kohman: J. Phys. Chem., 29, 1048 (1925).

TABLE III (continued)

Solubility of the Nitroanilines in Various Solvents, as interpolated at a Series of Temperatures, expressed in Terms of Mol-percentage.

Meta (m.p. 111.8°)

Solvent	t 140	120	110	100	90	80	70	60	50	40	30	25
Ideal				79.1	64.0	50.8	39.7	30.5	23.0			
acetone			96.8	78.9	64.1	52.4	43.7	36.9	31.2	26.3	21.7	19.5
ethyl acetate			96.1	76.0	59.2	46.0	35.6	28.2	23.4	20.0	17.3	16.1
chloroform			95.5	73.3	54.0	33.1	19.0	10.8	6.6	4.4	3.1	2.6
benzene			95.6	72.7	48.7	25.2	13.3	7.2	4.1	2.8	1.8	1.5
alcohol			94.9	73.0	49.5	25.8	14.1	8.5	5.6	4.1	2.9	2.4
ether			94.6	68.6	42.1	25.6	16.4	11.3	8.4	6.3	4.5	3.6
CCl_4				86.7	7.0							
water										0.23		0.12
$C_6H_5NO_2$			96.1	76.0	59.2	46.0	35.6	27.0	21.3	16.7	13.0	11.3
C_2Br_2			95.6	72.7	50.8	33.0	20.0	12.5	7.8			

Para (m.p. 147.5°)

Solvent	140	120	110	100	90	80	70	60	50	40	30	25
Ideal	89.5	65.8	56.1	47.3	39.8	33.3	27.6	22.8	18.6			
acetone	88.8	63.0	53.2	45.1	38.6	33.5	29.7	26.5	23.8			
ethyl acetate	87.1	56.5	44.6	35.8	28.6	22.9	18.8	15.8	13.4	11.4		
chloroform	86.5	51.0	29.8	16.1	8.8	5.3	3.6	2.5	1.8	1.3	1.0	0.8
benzene	84.8	40.9	16.8	8.4	4.3	2.6	1.7	1.2	0.8	0.6	0.4	0.3
alcohol	87.5	54.7	39.2	25.9	15.3	9.4	6.6	5.1	3.9	2.9	2.2	2.0
ether	85.6	32.4	12.7	7.9	5.7	4.7	3.8	3.4				
water										0.15		0.074
$C_6H_5NO_2$	87.1	59.0	48.6	39.2	31.2	24.6	19.3	14.9	11.7	9.3	7.5	6.7
C_2Br_2	84.8	46.2	30.9	18.8	11.0	6.5						

alcohol, whereas that of *para* in benzene is less than in alcohol, and the two solubility curves of the *meta* are practically coincident. It is thus evident that one can not set up an invariable sequence of liquids, arranged in order of solvent power over a group of crystalline substances, even for these three isomers which might well be supposed to resemble one another very closely in this regard.

This lack of definite sequence implies differences of behavior of the three isomers with respect to any particular solvent; and these differences were made evident in the course of our attempts to find a method of plotting such that the three curves for any one solvent could be superposed. In these attempts many pairs of variables were tried[1], but we were unable to discover any method, or any factor[2], which would enable us to derive the solubility of one isomer from that of another, except as a rough approximation. Nevertheless the curves so derived show comparatively little curvature and so such plots have some practical value; for if the curve for one isomer is known, the relation can be used to check, and to minimize the number of, the individual measurements of the solubility of the other two isomers.

The fact that these curves are apparently not superposable is evidence of a difference, from one isomer to another, in the mode of variation with temperature of the (differential) heat of solution in a given solvent[3]; and this can be shown directly by a plot of the relative slope of the log C vs. $1/T$ curve, for this slope is at any point proportional to the heat of solution. It may be possible to be more definite on this matter when work on other similar systems, now under way, is completed.

It appears however that, in any given solvent at a specified temperature, the isomer with the lowest melting temperature is most soluble, the highest melting the least soluble, when the equilibrium is between crystals and solution. On the other hand, Sidgwick and his collaborators have measured the solubility of similar groups of isomers as liquids in water and benzene, and find[4] that the vapor pressure and solubility relations in the liquid state are "in the majority of benzene derivatives very little influenced by the orientation of the substituents", but that "the solubility of the solids is largely determined by the crystalline forces, which themselves are greatly affected by the orientation". It appears therefore that the differences in solubility of the solid isomers are to be ascribed to the same factors which cause differences in their melting temperatures and heats of melting.

With respect to the question of the separation of the isomers from one another by a process of recrystallization, the general similarity of the groups of curves makes evident that the several solvents—with one exception, carbon tetrachloride—would be about equally effective. In any specific case, the solubility data readily enable one to make an estimate of the number of recrystallizations required to ensure purity, on the basis that the solubility of one isomer is not appreciably affected by the presence of another—an assumption which in such cases is in all probability not far from the truth. For instance, if we start with 100 mols benzene saturated at 60° with all three, we would have in solution 313.2 mols *ortho*, 7.8 mols *meta* and 1.2 mols *para*, corresponding to an initial mixture containing 97.2% *ortho*, 2.4% *meta*, 0.4% *para*; from the solution cooled to 25°, there would separate 301.5 mols *ortho*, 6.3 mols *meta* and 0.9 mols *para*, and the composition of the crystals would be about 97.7% *ortho*, 2.0% *meta* and 0.3% *para*. From this it is evident that this process (the amount of benzene used in each case being just sufficient to dissolve all of the ortho at 60°) would have to be repeated at least four or five times to insure pure crystals of *ortho*, the theoretical yield of which would be about three-fourths of the present initially. Moreover the number of recrystallizations required would change little with variation of the temperature limits, and within the group of solvents studied, carbon tetrachloride excepted; this material difference is brought out by Table IV.

---

[1] For instance, by plotting, for equal values of mol fraction in solution, t_o against t_m or t_p, or similarly Δt_o against Δt_m or Δt_p; or the corresponding values for each isomer, at a series of values of C, of the expression $\Delta H_A(1/T - 1/T_A)$, where ΔH_A is the heat of melting at the melting temperature T_A, a method which brings the ideal curves into substantial coincidence.

[2] Such as that proposed by Mortimer: J. Am. Chem. Soc., **45**, 633 (1923).

[3] This has been used by Sidgwick and his collaborators as a criterion of the nearness of the temperature at which the solution will separate into two liquid layers.

[4] Sidgwick and Callow: J. Chem. Soc. **125**, 529 (1924); q.v.

TABLE IV

Solubility of the Nitroanilines in Benzene and in Carbon Tetrachloride expressed as mols per 100 mols solvent.

	Benzene			CCl_4	
Temp.	*o*	*m*	*p*	*o*	*m*
25	11.7	1.5	0.3	2.0*	1.0*
40	44.2	2.9	0.6	4.8	1.4*
50	106.6	4.3	0.8	26.7	1.7*
60	313.2	7.8	1.2	283.1	2.0*

*Extrapolated and so less certain.

If 100 mols carbon tetrachloride are saturated with both *ortho* and *meta* at 60°, the resulting solution will contain 283.1 mols *ortho* and 2.0 mols *meta*; when this solution is cooled to 25°, 281.1 mols *ortho* and 1.0 mol *meta* will separate. Hence it is obvious that a second similar crystallization process would yield pure *ortho*, and in quantity almost equal to that originally present. There does not appear to be any way of predicting the fact that carbon tetrachloride is so much more effective than the other solvents in purifying *o*-nitroaniline from its isomers by recrystallization; but we may, with some assurance, infer that it would be similarly effective in some other similar cases, and recommend that carbon tetrachloride—which moreover is noninflammable and cheap—be tried out for this purpose in place of some of the solvents more commonly used.

It appears therefore that in general a number of recrystallizations would be necessary for the separation of, say, the *ortho* isomer from the other two, there being in this type of case no likelihood of appreciable solid solution. In many cases however there may be some admixture of a second *ortho* compound, and the two would form mix-crystals; under such circumstances the number of recrystallization processes necessary would clearly be much larger.

Summary

Solubility data, determined by a synthetic method, for the three isomeric nitroanilines in acetone, ethyl acetate, chloroform, benzene, alcohol, ether, carbon tetrachloride over a range of temperatures extending up to the respective melting temperatures, are presented and discussed. The respective solubilities in water and 95% alcohol at 25° and 40° have also been measured, Though the solubility curves are in general very similar, yet there are significant differences as between the three isomers.

REVERSIBLE PERMEABILITY OF MEMBRANES AND ITS RELATION TO CELL METABOLISM

BY CHARLES GURCHOT

Introductory

It is well-known that a living cell removed from its parent organism can be kept alive in the proper liquid medium. If, instead of a single cell, a community of cells or a piece of tissue is kept in a nutritive liquid, the tissue not only will be preserved but it will grow and proliferate. In other words, in its own small way, it behaves more or less as a complete organism as long as the medium remains constant and as long as the tissue remains the same as it was at the start. But the isolated cell behaves differently. Its isolation is tantamount to a physiological divorce in addition to an anatomical one for the cell appears to be permanently at rest and in this condition it is impermeable for almost everything which it ordinarily uses for food and to the products of its metabolism which are formed in the interior of the cell[1] "from the undissolved carbohydrate reserves, and also for inorganic salts and salts of organic acids". Naturally the cell cannot behave in this way when still a part of the original organism. Another significant phenomenon takes place after death. Then the cell behaves as an ordinary membrane which retains colloids only.

It seems fairly well established, now, that the cell is surrounded by a pellicle which functions as a semi-permeable membrane. Deductions from the second law of thermodynamics embodied in Willard Gibbs' principle show that all substances present in the cell and which lower its surface tension must concentrate at the periphery, that is at the interface between the cell contents and the surrounding medium[2]. It has been shown that the concentration of some bile salts may exceed the solubility[3]. Such substances will be deposited then as solid films enclosing the cell. One is forced to ask whether something does not take place in the mass of tissue which alters the permeability of the cell through something which is either stored or produced in cells en masse. Unfortunately it is impossible at the present time to exact an equivocal answer to this question from the cell directly, for the simple reason that the composition of cell membranes is not known. Yet previous considerations suggest that we ought to find in the membrane substances which lower the surface tension of water considerably. Such are the fatty compounds. Nor is it known what makes the membrane semi-permeable, let alone how the permeability is altered.

It is necessary to work backward, so to speak, and to proceed by analogy. It seems advisable therefore to consider the whole question of semi-permeable membranes and perhaps of membranes in general. Experiments must be made first on easily reproducible membranes of definite composition and for which the technique has been worked out already. Copper ferrocyanide offers a membrane of definite composition which in many ways behaves not unlike living semi-permeable membranes. Copper ferrocyanide has been the subject of painstaking investigations of which those of Walden[1] are among the most important. Walden investigated the action of many inorganic and organic salts and acids on several membranes without, however, observing to see whether any of the substances which passed through had a permanent effect. It is true that his method of procedure made such observation impossible. Walden always had the reagents with which he formed his membranes on each side of them. In this way the membranes were constantly regenerated and the observation of permanent injury was out of the question. This same mode of manipulation enabled Collander,[2] recently, to reach unwarranted conclusions regarding the behavior of living membranes.

---

[1] Bechhold: "Colloids in Biology and Medicine", 244 (1919).

[2] Bayliss: "Principles of General Physiology" (1918).

[3] Ramsden: Proc. Roy. Soc., 72, 156 (1904).

We are confident that, in order to pursue its metabolic functions, the cell must, in some way, change its permeability; and, in fact, we know that it does. The larval cells of Arenicola when in a state of contraction lose the pigment ordinarily present in the cells[3]. Pilocarpine makes certain cells more permeable, atropine makes them less permeable, to certain dyes[4]. The egg cell on fertilization and the muscle cell on contraction increase their electrical conductivity[5]. More than this we have evidence that permeability changes are reversible. One example will suffice. The seaweed Laminaria increases its electrical conductivity when immersed in a ca. 2.5% solution of pure sodium chloride. On adding a little calcium chloride to the solution Laminaria returns to normal conductivity without showing signs of permanent damage[6]. Clowes[7] offers an explanation which, although insufficient, is nevertheless an advance over previous ones. He compares the cell membrane to an oil-water emulsion in which soaps concentrate at the interface between oil and water and lower the surface tension of one or the other liquid depending on whether or not there is present an oil or a water-soluble soap. Clowes goes on to summarize Bancroft's explanation for emulsions as follows:—"soaps of monovalent cations being readily dispersed in water but not in oil form a film or diaphragm which is wetted more readily by water than by oil, consequently the surface tension is lower on the water than on the oil side. Since the area of the inside surface of a film surrounding a sphere is smaller than that of the outside surface, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of greater surface tension to a minimum as compared with that of lower surface tension. On the other hand a film composed of soaps of divalent or trivalent cations being freely dispersed in oil but not in water is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase". The process[1] "is dependent on the presence of a film of soap between the phases and it is interesting to note the powerful effect of sodium oleate in destroying red blood corpuscles". On the addition of calcium chloride the resulting water in oil emulsion "would be impermeable to water but permeable to substances soluble in oil. A change of the latter kind if complete would not give us the properties which the normal cell-membrane possesses". It would be permeable to water and its solutes only on reversal to the oil in water emulsion. Such a membrane would be entirely too labile to enable the cell to manifest the osmotic pressure which it has actually. It is perhaps better to conceive of the cell membrane as a more or less rigid colloidal suspension, irreversible as we understand an emulsion to be reversible, but, as we shall see later, possessing a reversibility of its own. We shall see also that the degree of permeability can be altered in such a membrane.

---

[1] Z. physik. Chem. **10**, 699 (1892).

[2] Kolloidchem. Beihefte, **20**, 273 (1925).

[3] Lillie: Am. J. Physiol. **37**, 764 (1913).

[4] Garmus: Z. Biol. **58**, 185 (1912).

[5] McClendon: Am. J. Physiol., **27**, 240 (1910); **29**, 302 (1912).

[6] Science, (2) **34**, 187 (1911).

[7] J. Phys. Chem., **20**, 407 (1916).

Another interesting feature of the work of Clowes is the analogy which is drawn between the elongated drop stage, in the course of the reversal of the emulsion, when the dispersing liquid flows as through narrow channels, and the porous sieve-like character of the copper ferrocyanide membrane as conceived by Traube[2]. A great deal has been done to prove that water flows through a copper ferrocyanide membrane as it would through a series of capillary tubes.[3] Poiseuille's equation[4] has been called upon to prove this:

$$Q = \frac{KD^4PT}{L}$$

where Q is the amount of liquid, K a constant for a definite temperature, D the diameter of the pores, P the pressure applied, and L the length of the capillaries. From this equation values have been calculated for the diameter of the pores. It is unfortunate that Poiseuille's equation should have been misused in this way. The equation expresses exactly the results of motion of a viscous fluid through pipes of circular cross-section. It is assumed that the velocity is everywhere perpendicular to the cross-section of the pipe and it has been pointed out by Lamb that if any appreciable amount of slipping at the boundary of the pipes, used by Poiseuille, took place a deviation from the law of the fourth power of the diameter would become apparent. It becomes perfectly clear, therefore, that the difference in pressure between the inlet and the outlet of the pipe or tube is not an accurate measure of the pressure gradient because some of this pressure difference is required to give kinetic energy of motion to the water in the eddy currents which will be formed whenever the diameter of the pipe or tube is not uniform throughout. It is more than probable that this state of affairs obtains in the case of semi-permeable membranes.

---

[1] Bayliss: "Third Report on Colloid Chemistry", 4 (1921).

[2] Archiv für Anatomie, **1867**, 67.

[3] Bartell: J. Phys. Chem. **15**, 659 (1911); **16**, 318 (1912).

[4] Poiseuille: Compt. rend. **11**, (1840); **12**, (1841).

In other words if the equation for Bartell's membranes contained the term D raised to some other power than the fourth his results would have been the same. But as semi-permeable membranes generally operate at approximately atmospheric pressure and especially in the presence of electrolytes it might have been better to employ Fick's diffusion equation:

$\frac{dS}{dt} = k\,q\frac{dC}{dX}$ where dS/dt is the rate of flow, *k* the temperature coefficient, *q* the cross-section of the pores, dC/dX the rate of change in concentration of the diffusing solution. But after all has been said there is no reason to suppose that a semi-permeable membrane does not behave as if it were porous. After all, inter-molecular spaces are only a special type of pores. But we know that other factors, such as selective adsorption, affect the permeability of a membrane. It follows from this that both Poiseuille's and Fick's equations are useless to express the true diameter of pores even if it is granted that we have to deal with uniform capillaries. This we know is not true. Consequently all we can say is that copper ferrocyanide is porous. We know that this is vague to say the least. We also know that the statement does not mean anything for, strictly speaking, the water membrane between chloroform and ether is porous also. Attempts have been made to prove the copper ferrocyanide membrane to be an atomic sieve from the fact that progressively larger molecules diffused with increasing difficulty. Such a simple view is entirely inadequate at the present time. There is evidence to show that a copper ferrocyanide membrane does not work as a static system but rather as a dynamic one.

When Czapek[1] exposed cells of Echeveria to the action of various alcohols he noticed that an exosmosis took place of the tannin present in the cells. For methyl alcohol the critical concentration at 15-19°C. was about 15% by volume, for ethyl 10-11%, propyl 4-5%, butyl 1-2%, amyl 0.5%. Because the above solutions possessed a surface tension of about 68% that for pure water Czapek concluded that the surface tension lowering was responsible for the exosmosis, 68% of the value for water being the critical tension. This was as far as Czapek ventured. Had he known that tannin exists in colloidal solution he might have guessed that the exosmosis was due to coagulation of the cell membrane. Czapek found also that his plant cells gave the exosmose reaction with various organic and inorganic acids for concentrations exceeding N/6400. This was undoubtedly another case of coagulation owing to the adsorption of hydrogen ions by the cell membrane.

In 1906 Barlow[2], in the course of a series of osmotic pressure measurements through copper ferrocyanide, observed that the addition of alcohol to the outside solution caused a lowering of the osmotic pressure. Fearing that with alcohol in great excess the sign of the osmotic current might change, Barlow looked upon this phenomenon as an unfortunate incident—the alcohol having spoiled his membrane.

---

[1] Ber. deutsch. botan. Gaz. 28, 159 (1910).

[2] Phil. Mag. (6) 10, 1; 11, 505 (1906).

The whole question of membrane action seems to involve selective adsorption and coagulation; and the natural corollary is that the coagulation is reversible. There is no question that an investigation in this direction will throw some light at least on the behavior of cell membranes. In fact it seems very probable that our views on membrane action in general must undergo considerable revision.

The experiments described in the following pages will show that a copper ferrocyanide membrane behaves as a colloidal film analogous to a colloidal sol. It can be coagulated and it can also be peptized. On the other hand the peculiar spatial relations of a film in contrast to a sol make the consequences arising from the analogous behavior of the former very significant when we consider the reactions of living membranes. Such a film possesses, for example, a certain amount of rigidity and inertia which, to be sure, are essential if in the cell the film is to play the part of metabolic censor, so to speak. But as we shall see later, such properties make it very difficult to prove the analogy by experiment. If a continuous film—it is better to say a film with very fine interstices—can be converted at will into a sieve whose meshes can be closed when necessary we have here an answer to the question why a substance which ordinarily does not pass through a membrane will do so, nevertheless, at certain times. The antagonistic action of a peptizing agent toward a coagulating agent will enable us to explain the sodium-calcium antagonism in living cells. Of course it must not be expected that sodium and calcium will be antagonistic for copper ferrocyanide. There is every reason why they should not be. The antagonism will be of a different kind. After all, whatever may be the composition of cell membranes we are quite certain it is not copper ferrocyanide.

Experimental

Copper ferrocyanide membranes were made by a modification of Collander's method. Glass tubes were used, 3cm. in diameter and 10cm. long. One end of each tube was ground and covered with a layer of cheese cloth to serve as a support for the membrane. This end was dipped into a warm ten per cent solution of gelatine freed from air bubbles by filtering through sand. The gelatine solution should not be heated higher than 40°C. Instead of a ten per cent a fifteen percent solution of gelatine may be used. It will give a firmer support and will be very much less liable to damage; but at the same time the membrane will take longer to be deposited in the denser gelatine layer where diffusion must take place more slowly. The gelatine was allowed to set to a stiff jelly on the cheese cloth, the tube being held downward after the excess of gelatine had been removed. It was found convenient to hasten the jellying by blowing compressed air on the tube for about a half minute. It is immaterial if a few air bubbles persist in the gelatine film at this stage. When the gelatine film was a firm jelly, 2cc of the same gelatine solution, freed from air bubbles, were introduced inside the tube on top of the first gelatine layer. It is important that there are no bubbles in this layer. The reason is, of course, that a bubble in the plane of the deposited membrane will destroy its continuity. This upper layer was allowed to set to a stiff jelly also and it was hardened for twenty-four hours in a two percent solution of formaldehyde. The gelatine tubes were washed free of formaldehyde in several changes of distilled water, the tubes being allowed to remain about two hours in each change of water. They were suspended in tumblers or in beakers by means of two copper strips, about one centimeter wide, pinched at each end with paper clips. A small piece of Gooch rubber tubing at the top of each tube prevented the latter from slipping through the copper strips whose fastened ends rested on the edge of the tumbler or the beaker. A fresh solution containing 0.02 mols potassium ferrocranide was placed outside and a solution containing 0.02 mols copper sulphate was put inside the tube. In about a half hour copper ferrocyanide began to form near the inner gelatine surface as a uniform brown membrane. The reaction was allowed to go on for twenty-four hours if a ten percent gelatine solution was used. The reaction required forty-eight hours in case a fifteen percent gelatine solution was employed. After each membrane had been washed free of the reagents it was tested by putting a one percent solution of cane sugar inside the tube and distilled water outside. If there was no test for sugar in the outside water after sixteen hours, the membrane was considered satisfactory. The above procedure was carried out at room temperature, that is to say about 20°C. As a result never more than about two-thirds of the membranes made were found satisfactory. But as we shall see later certain considerations necessitated a change in method, and when the membranes were formed and kept at 8°C. the yield was one hundred percent and they lasted much longer. It is sometimes advised that thymol be added to the gelatine solution to prevent the membrane from being destroyed in the first process by bacteria which liquefy gelatine. This added inconvenience is unnecessary provided cleanliness is observed. There are bacteria which attack the copper ferrocyanide film and create holes in it. But by working at 8°C. this contingency is prevented also.

Coagulation with Propyl Alcohol

The first thing to be investigated was the permanent action of alcohols on the copper ferrocyanide film. For this, twelve series of two tubes were used. In every test it must be assumed that three membranes were used unless it is stated otherwise. Propyl alcohol of varied strengths was put in each tube. Distilled water was put outside. At the end of sixteen hours, after the membranes had been washed thoroughly, a one percent solution of sugar was introduced inside each tube. The water outside was tested for the presence of sugar sixteen hours later. The semi-quantitative results are given in Table I.

It is interesting to note that greater strengths of alcohol were not followed with a more abundant Fehling precipitate. This is just what should be expected if the copper ferrocyanide film is conceived to be a close aggregation of colloidal particles each surrounded with a film of adsorbed water. On addition of alcohol the individual particles—or the small groups—unite to form larger aggregates. This is followed by an increase in porosity sufficient to let

TABLE I

Membranes	Propyl alcohol % by volume	Precipitate with Fehling's solution
1	1	Faint trace
2	1.5	Large trace
3	2.0	Moderate
4	2.5	Moderate
5	3.0	Large trace
6	3.5	Large trace
7	4.0	Moderate
8	4.5	Moderate
9	5.0	Trace
10	5.5	Trace
11	6.0	Trace

sugar through. But it must be much more difficult for these aggregates to unite and form still larger ones. To accomplish this it may be necessary to use much higher concentrations of alcohol. It is even possible that the resistance of the gelatine will prevent further coagulation even then.

If the coagulation of the membrane is an effect of the decrease in surface tension brought about by adding alcohol to water it is conceivable that coagulation might be reversed by bringing the membrane in contact with a liquid of higher surface tension, namely pure water. Accordingly the alcohol-treated membranes were exposed to water about forty-eight hours. At the end of that time no reversibility had taken place. The membranes were still permeable to sugar. A second treatment with water gave no better results. This, of course, does not prove that surface tension is not a factor in the coagulation of copper ferrocyanide.

Coagulation with Methyl Alcohol

The experiments were repeated, this time methyl alcohol was used because it is available for smaller changes of surface tension than propyl alcohol. The alcohol and the sugar were put inside the tube at the same time. The results are given in Table II.

TABLE II

Alcohol inside tube; sugar solution 1%—exposure 16 hours; room temperature 20°C.

Membrane	% Methyl alcohol	Fehling's precipitate
1	0.1	None
2	0.2	None
3	0.3	None
4	0.4	None
5	0.6	None
6	0.8	None
7	1.0	None
8	1.5	Faint trace

The minimal concentration for methyl alcohol seems to be about 1.5%

The experiments were repeated with methyl alcohol outside the tube and the 1% sugar solution inside the tube. The results are given in Table III.

TABLE III

Alcohol outside tube; sugar solution 1% inside tube; exposure 16 hours; room temperature 20°C.

Membrane	% Methyl alcohol	Fehling's precipitate
1	0.1	None
2	0.5	None
3	1.0	None
4	1.5	None
5	2.0	Trace

The noteworthy difference is that more alcohol was necessary to coagulate the membrane here than when both sugar and alcohol were on the same side. This is not surprising. Since sugar is insoluble in pure alcohol the addition of the former to an aqueous alcoholic solution must raise the partial pressure of the alcohol. In other words when sugar and alcohol are on the same side of the tube alcohol behaves as if it were more concentrated.

Both series of membranes were also given the water treatments of forty-eight hours each, but no recovery took place. If, as was suggested, coagulation is a surface tension effect—which is doubtful as we shall see later—reversibility must nevertheless be difficult to obtain inside the gelatine support. Here something must be said about the question of minimal concentration. It is not devoid of ambiguity because just as soon as a membrane becomes ever so slightly permeable to sugar the permeability will not be apparent until the membrane has been exposed to sugar for a sufficient length of time. In addition to this a very long exposure to very dilute alcohol will show the same results as a correspondingly short exposure to more concentrated alcohol. The time must therefore be fixed arbitrarily, and the minimal concentration must be allowed to remain a function of the time, the temperature remaining constant. It is practically impossible, consequently, to know just exactly when a membrane becomes permeable to sugar. And in addition to this it is not at all surprising that reversibility, if it can be obtained at all, by increasing surface tension, is difficult to accomplish.

Coagulation and Reversibility of Copper Ferrocyanide Sol

A corollary from the above experiments is that methyl alcohol must coagulate a copper ferrocyanide sol. But the precipitation of the sol proved to be much less sensitive than the test for the permeability of the membrane. In the case of the former the coagulated particles must gather in groups large enough to be seen with the naked eye. Under a microscope the precipitation would undoubtedly be more sensitive. The experiments were carried out in groups of three test tubes. The colloidal solution of copper ferrocyanide was made from very dilute reagents. One gram of potassium ferrocyanide and one gram of copper sulphate, each dissolved in 3000 cc of distilled water, were allowed to react. A very stable brown colloidal solution was obtained which showed no sign of having precipitated after standing for two weeks. The results are given in Table IV.

TABLE IV

Group	Volume	% Methyl alcohol	Time	Degree of precipitation
1	15cc	0.10	2 days	—
2	15cc	0.22	2 days	—
3	15cc	0.30	2 days	—
4	15cc	0.40	2 days	—
5	15cc	0.45	2 days	—
6	15cc	0.50	2 days	—
7	15cc	0.55	2 days	—
8	15cc	0.60	2 days	—
9	15cc	0.65	2 days	—
10	15cc	0.70	2 days	—
11	15cc	0.75	2 days	—
12	15cc	0.80	2 days	—
13	15cc	0.85	2 days	—
14	15cc	0.90	2 days	—
15	15cc	0.95	2 days	—
16	15cc	1.00	2 days	—
17	15cc	1.05	2 days	—
18	15cc	1.10	2 days	—
19	15cc	1.18	2 days	—
20	15cc	1.28	2 days	—
21	15cc	1.32	2 days	—
22	15cc	1.36	2 days	—
23	15cc	1.41	2 days	—
24	15cc	1.46	2 days	—
25	15cc	1.50	2 days	—
26	15cc	1.55	2 days	—
27	15cc	1.59	2 days	—
28	15cc	1.64	2 days	—
29	15cc	1.68	2 days	—
30	15cc	1.73	2 days	—
31	15cc	1.77	2 days	—
32	15cc	1.82	2 days	—
33	15cc	1.86	2 days	—
34	15cc	1.91	2 days	—
35	15cc	1.96	2 days	—
36	15cc	1.96	2 days	—
37	15cc	2.44	2 days	—
38	15cc	2.91	2 days	—

TABLE IV (continued)

Group	Volume	% Methyl alcohol	Time	Degree of precipitation
39	15cc	3.40	2 days	−
40	15cc	3.85	2 days	−
41	15cc	4.30	2 days	−
42	15cc	4.75	2 days	?
43	15cc	5.20	2 days	−
44	15cc	5.65	2 days	−
45	15cc	6.10	2 days	−
46	15cc	6.50	2 days	−
47	15cc	7.00	2 days	−
48	15cc	7.40	2 days	−
49	15cc	7.80	2 days	−
50	15cc	8.25	2 days	−
51	15cc	10.00	2 days	−
52	15cc	15.00	2 days	−
53	15cc	20.00	2 dyas	−
54	51cc	25.00	2 days	−
55	15cc	30.00	2 days	−
56	15cc	35.00	2 days	−
57	15cc	40.00	2 days	+
58	15cc	45.00	2 days	++
59	15cc	48.00	2 days	+++
60	15cc	50.00	2 days	++++

From the three tubes containing forty percent alcohol 14.5cc of the colorless supernatant liquid were pipetted off and substituted with the same amount of distilled water. The flocculated copper ferrocyanide was peptized immediately and had not visibly precipitated again after standing one week. This is clearly a case of reversibility without the encumbrance of a membrane. Here it may be argued that reversibility resulted from the increase in surface tension when water was substituted for aqueous alcohol. To say this is to argue *post hoc ergo propter hoc.* All we know from observation is that reversal was preceded by a surface tension increase. This is very different from saying that reversal was caused by the increase of surface tension.

It was pointed out above that the coagulation of copper ferrocyanide sol with about 40% alcohol is not a sensitive test. Yet a method was available whereby the sol could be made just as sensitive, if not more so, as its corresponding membrane to the action of dilute alcohol. But to make the phenomenon more general two other negative sols were used instead, namely sulphur and arsenious sulphide. Both sols were prepared by a method of condensation the details of which can be found in almost any book of laboratory methods in colloid chemistry.

The experimental procedure was to add just enough of some flocculating agent not to precipitate the sol and then to determine the quantity of alcohol—

ethyl alcohol was used—necessary to flocculate it. The experiments were carried out in test tubes disposed in series of four with several tubes kept as controls, Tables V-VI.

TABLE V

Arsenious Sulphide flocculated with M/8 Sodium Chloride

Volume of sol 5cc. Time 24 hours.

M/8 NaCl	Reaction
1cc	None
1.5cc	None
2.0cc	Marked turbidity
2.5cc	Marked turbidity
3.0cc	Marked turbidity
3.5cc	Granular precipitate

Three tubes to which 1.5cc M/8 NaCl had been added were treated with 0.03cc ethyl alcohol (about 0.5%). The fourth was kept as control. After 24 hours the three tubes treated were turbid. The fourth remained clear.

TABLE VI

Sulphur flocculated with N/400 Calcium Chloride

Volume of sol 5cc. Time 24 hours.

N/400 $CaCl_2$	Reaction
0.1cc	None
0.3cc	None
0.5cc	None
0.7cc	Slight turbidity
0.9cc	Marked turbidity

Three tubes to which 0.5cc N/400 calcium chloride had been added were treated with 0.02cc ethyl alcohol. The fourth tube was kept as control. After standing for 24 hours the three tubes were turbid while the fourth remained clear.

The results of these two series of experiments show that under the proper conditions sols can be precipitated by very dilute alcohols. Arsenious sulphide required about 0.5% and sulphur about 0.4% ethyl alcohol.

Some qualitative experiments were performed with glucose, sugar and ½% glycerin. A dilute sulphur sol was flocculated after 24 hours by glucose and sugar syrups and also by the glycerin solution.

Coagulation with Acetic Acid

In order to confirm Walden's results with organic acids experiments were made also with copper ferrocyanide membranes and solutions of acetic acid. Sugar and acetic acid were placed inside the tubes and a solution of blue litmus was placed outside. The litmus turned red after two hours and the outside solution was tested for sugar. The results appear in Table VII.

TABLE VII

% Acetic Acid	Fehling Precipitate
0.2	None
0.5	Faint trace
1.0	Trace
1.5	Moderate

The critical concentration seems to be around 0.5% acid. Here again an attempt was made to effect a reversal by treating the membrane with water. No reversal was obtained. Then, since sodium hydroxide should peptize a negative sol, it was tried as a reversing agent. But here the membranes reversed entirely too much. A fifth-normal solution of NaOH entirely peptized the copper ferrocyanide membranes in six hours. The same result was accomplished when a N/50 NaOH solution was used. Then the membranes were exposed to a N/5 NaOH solution for twenty minutes. They turned purplish brown. They were then washed and put aside. Two hours later the gelatine support was detached from the glass and the membranes floated free. Some were then exposed to a N/500 NaOH for thirty-six hours. They showed no visible alteration but they remained permeable to sugar. In other words no recovery from coagulation took place.

Further Attempts at Reversal

Several membranes which had been coagulated previously with methyl alcohol were treated for twenty-four hours with a saturated solution of sodium chloride. The solution was placed on both sides of the membranes so as to preclude dilution by osmosis if pure water was put on one side. Some of the membranes showed partial recovery. In other words the Fehling precipitate was much less abundant than before the salt treatment. But on standing for twelve hours they were again tested for sugar permeability. This time the cuprous oxide precipitate was as abundant as it had been before the salt treatment. If there was no large experimental error, the observation is an interesting one perhaps; but as far as indicating that reversibility took place it probably means nothing at all. At this stage it seemed almost a hopeless venture to attempt to reverse coagulated membranes although the thing must be, without a doubt, theoretically possible. On the other hand, looking at it from a different point of view, reversibility might not be so essential. In plant and animal cells the membrane-forming materials might be supplied continually. Recent work has thrown much doubt on this idea. Still if living membranes could reverse their increased permeability and if they availed themselves of the membrane-forming materials only in case of emergency if, at all, the procedure would be far more desirable in the economy of life. It seemed rather a pity that the latter situation should not prevail. It probably does in fact, as we shall see later.

Effect of the Presence of Membrane-forming Reagents

Accordingly, some experiments were tried with copper sulphate on one side and potassium ferrocyanide on the other side of the membrane and of the same concentration as the reagents used in making the membranes. Controls, without any of the reagents on either side, were used in every case. Although the contents on the inside of the tubes varied, the outside solution did not vary from one experiment to another. In every case potassium ferrocyanide and distilled water only were present outside the membranes. The presence of potassium ferrocyanide interfered, of course, with the detection of sugar. The hydrochloric acid which was added to hydrolyze the sucrose reacted with potassium ferrocyanide to form ferrocyanic acid. This came down as a white precipitate and in addition to using up the HCl obscured any other precipitate which might form. As a result the procedure summarized below was adopted. It was found to work perfectly well on known samples:

1. Precipitated $K_4Fe(CN)_6$ with slightly more than half its volume 0.04 molar copper sulphate.
2. Disregarded brown precipitate, added 2 drops conc. HCl and boiled.
3. Added 2cc of a saturated solution of $NaHCO_3$, boiled off CO_2 excess.
4. Allowed copper ferrocyanide precipitate to settle.
5. Pipetted clear supernatant liquid.
6. Boiled with Fehling's solution in the usual way.

The results of the experiments are given in Table VIII.

TABLE VIII

Outside $K_4Fe(CN)_6$	$CuSO_4$	$CuCl_2$	Inside CH_3OH	$NaCl$	$CaCl_2$	Sugar	Time Reaction	
0 02M	0.02M		3%			1%	48 hrs	—
0 02M	0.02M		5%			2%	72 hrs	—
0.02M	0.02M		10%			2%	24 hrs	—
0.02M	0.02M			5%		1%	48 hrs	—
0.02M	0.02M			25%		2%	24 hrs	—
0.02M		0.02M		5%	.25%	1%	48 hrs	—
0.02M		0.02M		25%	1.25%	2%	48 hrs	—
0.02M		0.02M			5%	1%	48 hrs	—
0.02M		0 02M			12.5%	2%	48 hrs	—
0.02M		0.02M	2%		1%	1%	48 hrs	—
0.02M		0.02M	5%		5%	2%	48 hrs	—
				5%		2%	10 hrs	+

Only the last experiment, where no membrane-forming reagents were used, showed the membrane to have coagulated. All other tests showed negative results, even though in the case of sodium chloride the salt was found outside the membrane. Not so with calcium chloride. Cupric chloride was used instead of copper sulphate to prevent the formation of calcium sulphate.

Critical Concentrations of Alcohols and Reversal of Coagulation

The next part of this investigation was carried out during cold weather when the temperature of the heated laboratory rose to 26°C. Indeed it reached 27°C. more than once. This circumstance was very unfortunate in one way, but it proved very fortunate in another way. First of all, the copper ferrocyanide membranes did not work properly. The yield was very small. Sometimes every new membrane was permeable to sugar before having been used at all. It was thought that the gelatine softened and impaired the membrane support. Various schemes were tried to find some twenty-seven degree-proof support for the membrane but none was found satisfactory. Among other things agar-agar was tried. Owing to the fact that agar is soluble in water only at about 85°C. it needs no tanning treatment and would make an ideal support if it were not that it shrinks on cooling and loosens itself from the glass tubes. This loosening did not take place however until the copper ferrocyanide membrane was deposited. This loosened membrane was, of course, useless for diffusion experiments, but its structure could be examined in detail. It was found that the membrane had formed about 1.5mm below the inside surface, and that the agar above the membrane was colored brown for a distance of about 1mm. This was clearly a case of peptization of copper ferrocyanide in agar and as far as the membrane itself was concerned it appeared intact. The peptizing agent could be only copper sulphate. On the potassium ferrocyanide side the membrane was not peptized visibly. There is nothing strange in this for the silver halides are peptized by silver nitrate and the corresponding potassium halide. Here was a suggestion for one more attempt at reversibility. But in the mean time stable membranes had to be made. This was finally done by using a 15% gelatine solution to begin with, forming the membranes, and keeping them at all times, in low temperature thermostats. Several were made, tap water being used as the cooling medium. All winter the temperature in the thermostats varied between 6 and 8 degrees centigrade. Once or twice it rose to ten degrees but never higher. Another possibility not to be overlooked was that copper ferrocyanide membranes might be coagulated by pure water at comparatively low temperatures. But before heat coagulation was investigated in addition to a possible reversal with copper sulphate it was necessary to determine the critical concentration for several of the alcohols used by Czapek and see what relation they bore to the critical concentrations which he obtained as a result of his experiments on exosmosis. The four alcohols chosen were methyl, ethyl, propyl and amyl. In addition to this, since it was found that sodium chloride coagulated copper ferrocyanide its critical concentration should also be determined and compared with that of potassium chloride and calcium chloride; three salts which play a very important part in the metabolism of living cells,Table IX.

TABLE IX

Concentration	Sugar test	Estimate of critical concentration from appearances of ppts.
	Methyl Alcohol	
0.1%	negative	
1.5%	positive	Below 1.5%
	Ethyl Alcohol	
0.4%	negative	
0.6%	positive	Between .5—.6%
	Propyl Alcohol	
.13%	negative	
.20%	positive	About 2%
	Amyl Alcohol	
.08%	negative	
.10%	negative	
.17%	negative	
20%	positive	Below 2%
	Sodium Chloride	
0.1%	negative	
1.5%	negative	
2.0%	positive	About 2%
	Potassium Chloride	
0.1%	negative	
1.5%	negative	
2.0%	positive	About 2%
	Calcium Chloride	
0.5%	negative	
0.1%	positive	
1.5%	positive	Below 1%

It is interesting to note that no calcium was found in the outside water for the 0.5% tube. A trace of calcium chloride was found for the 1% tube; and the 1.5% tube gave a very decided test for both calcium and chloride in the outside water.

The reversibility experiments with copper sulphate were much more successful than the previous attempts. The results were decisive except perhaps in the case of ethyl alcohol where a more concentrated copper sulphate solution had to be used in order to effect a reversal. Three tubes were used in every case for each alcohol. The sugar tests were negative, Table X.

There are, of course, many experiments which might have been tried on the basis of the results given above. Time did not permit it, however. The peptizing action of copper sulphate on precipitated copper ferrocyanide sols

TABLE X

Coagulating agent	Concentration of copper sulphate	Number of tubes which recovered
Methyl alcohol	0.02M	3
Ethyl alcohol	0.02M	0
Ethyl alcohol	0.20M	2
Propyl alcohol	0.02M	3
Amyl alcohol	0.02M	3

might have been tried as an analogy to the peptization of silver halide precipitates. Also, the addition of copper sulphate to sodium chloride solution should raise the latter's coagulating concentration. The same should be true of copper sulphate and alcohols.

Another interesting suggestion was furnished from work done with colloidal solutions of ferric oxide (Briggs and Vannoy 1925). It was found that concentrated solutions of calcium chloride (above 30%) peptized ferric oxide formed from ferric chloride and ammonium hydroxide, producing a negative sol. But when coagulated copper ferrocyanide membranes were treated with syrupy calcium chloride solution (70%) not only did they not recover, but after the treatment they allowed far more sugar to go through than before.

Coagulation by Heat

For these experiments a small oven was used jacketed with running water and heated with a bunsen flame. The temperature varied within one degree. The net result obtained was that copper ferrocyanide membranes were coagulated by pure water between 23 and 24°C.—more probably 24°C. The futility of working with such membranes at room temperature of 26°C. becomes apparent at once. There is no doubt, of course, that when the temperature of the water is raised its surface tension is lowered; and coagulation of copper ferrocyanide at 23 or 24 degrees may have been brought about by the surface tension lowering. But it is also true that adsorption decreases with rise of temperature, that consequently the film of adsorbed water around the membrane particles is not as thick as it was before which is the same as saying that effectual pores may be formed allowing such things as sugar to go through which would otherwise be retained by virtue of the negative adsorption exhibited by copper ferrocyanide towards sugar. This is all the more convincing when we consider the lack of agreement between the surface tensions of several alcohols and water at 23.5°C, Table XI.

TABLE XI

Reagent	Concentration	Surface tension	% Lowering of surface tension against HOH at 8°C
Methyl alc.	1.5%	66.5 dynes	11%
Ethyl alc.	5-6%	67 dynes	10%
Amyl alc.	.2%	68.5 dynes	8%
Water 23.5°		71.8 dynes	4%
Water 8°		74.5 dynes	0%

Conclusions

Before discussing the relation between the experimental results and the behavior of cell membranes we must take up the question of coagulation from the point of view of semi-permeable membranes in general of the type represented by copper ferrocyanide. There is no question about the external appearance of copper ferrocyanide membranes deposited in gelatin. Microscopic examination undertaken by means of objectives of high resolving power (N. A. 1.4, Zeiss Apochromat) showed beyond a doubt that the membrane is granular in character. Separate grains or groups of them are present and make up the entire area. Their size could not be measured, of course, owing to the presence of overlapping diffraction halos; and it is difficult to see how Tinker[1] in 1916 calculated the size of copper ferrocyanide particles by means of the wretched photographs which he published. Since copper ferrocyanide forms a hydrosol each particle or group must possess a layer of adsorbed water. When alcohol is added there are three possibilities: First, coagulation is brought about by a decrease in surface tension. This explanation is tenable only if we consider the copper ferrocyanide film to be a continuous membrane like rubber. We know that this is not the case. But if we consider the membrane to be granular it is not clear how surface tension decrease can be a factor in coagulation. The particles should tend to break up into still smaller ones and in the end a finer grained membrane would result which if anything should be less permeable than before. Second, if coagulation is due to selective adsorption it may involve the entire alcohol molecule or the positive radical. But when a sol coagulates it does so because the charge on each particle which keeps all particles apart is reduced or neutralized and the particles agglomerate. In other words the adsorption of alcohol by a negatively charged sol like copper ferrocyanide must entail a reduction or neutralization of its negative charge.

The electrically neutral aggregates can unite to form larger units and finally one large coagulum will result. The difference between such a final aggregation and the original one is that its area is smaller, it is more compact and water, both adsorbed and not, will be present around it. At no time then is coagulation reversed as in the case of decreased surface tension. The last possibility is the removal of water of hydration from the supposedly continuous hydrated copper ferrocyanide membrane with consequent shrinkage and the formation of cracks which would render the membrane permeable to things to which it is ordinarily impermeable. It was this consideration which prompted Walden and others to retain the membrane-forming reagents on both sides of the copper ferrocyanide. But if coagulation were indeed a question of the removal of water of hydration—the fact that copper ferrocyanide is granular alone throws a damper over the hydration theory—the cracks formed in its substance could not be obliterated by peptizing with copper sulphate. It may be argued that copper sulphate did not peptize the membrane but that instead it reacted with adsorbed potassium ferrocyanide which could not be washed out and the cracks were healed by the reprecipitation of copper ferrocyanide. The microscopic examination of the membrane in agar which showed the presence of peptized membrane material militates against the strength of this argument in addition to the fact that we know such things as silver halides to be peptized by their own reagents. Unless something has been left out of consideration we can be fairly certain so far that coagulation is a question of selective adsorption, washing out the alcohol with water will not necessarily peptize the membrane and thereby make it impermeable to sugar once more. The coagulated particles merely take collectively their film of adsorbed water and the spaces remain through which sugar can pass. The rigidity of the gelatine support is alone responsible for this because we have seen that in test tubes a coagulated copper ferrocyanide sol could be repeptized by the addition of water. In the latter case the addition of water was tantamount to a mechanical disintegration for the flocculated copper ferrocyanide was still in a very fine state of subdivision. The amount of alcohol remaining after peptization of the sol was 1.3% which is the amount just necessary to make a membrane permeable to sugar. But, as it was suggested before, the degree of coagulation could not be appreciated possibly since 40% alcohol was necessary to make the phenomenon visible in a test tube to the naked eye. Then there is the question of coagulation by heat. If the membrane were a continuous one it is difficult to see how a decrease in the surface tension of about one dyne produced by an increase of a few degrees—it must be remembered that at 20°C. successful experiments were performed—should make it permeable to sugar, although we must admit that the thing would not be impossible. But if the phenomenon is connected with surface tension then there must be a critical tension when a continuous membrane becomes discontinuous—forms drops in other words. The evidence given above shows that there is not. Alcohols acted at about 90% the original tension, water at 96%. If we must postulate a toxic action certainly we cannot blame it on the water. The alcohols cannot be blamed either because the discrepancy between methyl, ethyl, normal propyl, iso-propyl, butyl, iso-butyl, amyl and allyl and tertiary butyl is attributed to a toxic action on the part of the latter two. But, after all, the microscopic evidence is unequivocal enough.

---

[1] Proc. Roy. Soc., 92A, 357 (1916).

We cannot say that the copper ferrocyanide membrane operates like a sieve because such a statement is only a small part of the story. It may act as a sieve for sodium and potassium chloride only under certain conditions because if the salts are present in dilute enough solution they will go through the membrane without coagulating it. This can be easily explained. If the adsorption isotherm for chloride ion in the presence of sodium ion, for example, reaches a constant value much before the isotherm for sodium ion in the presence of chloride, there must be a concentration for which both ions will be adsorbed equally. Since sodium chloride is soluble in water it will dissolve in the adsorbed water layer, under such conditions, and pass through the membrane without coagulating it. At higher concentrations the sodium ion will be adsorbed more and more whereas the chloride ion will not. As a result there must come a point when the membrane will no longer be negative and coagulation will ensue. From this point on sugar will pass through the membrane, provided the membrane-forming reagents are absent. Sugar molecules which are adsorbed negatively will not go through therefore, until effective pores have been formed. This will not happen as long as both the membrane-forming reagents are present.

The case of calcium chloride is interesting. Walden[1] found that sometimes it did go through and at other times it did not. This happened when he used copper acetate one on side and potassium ferrocyanide on the other. Here Walden must have been using calcium chloride solutions of somewhere near the critical concentration below which it would not go through copper ferrocyanide when the membrane-forming reagents were present. In fact earlier in his paper Walden says that his diffusing solutions were *about* normal. But finally he succeeded in preventing his calcium chloride solutions from going through when, instead of copper acetate, he used copper nitrate on one side of the membrane. When this is correlated with the results obtained from experiments on reversibility with copper sulphate, described earlier in the present paper the explanation is easy. Copper ferrocyanide probably adsorbs the nitrate ion more readily than it does the acetate ion. Consequently the membrane is kept negative, and for the same concentration of calcium chloride in both cases the latter will not go through in the presence of copper nitrate.

With calcium chloride the adsorption isotherm reaches its constant value probably at such a low concentration that calcium chloride will pass through the membrane in negligible amounts only without coagulating it. In other words calcium chloride will not pass through the membrane until it coagulates it. And so we find that as soon as we can obtain a test for calcium chloride in the outside water sugar is present there also.

Finally we can say that a substance in solution will go through a membrane by osmosis when like sodium chloride it will go through without producing coagulation. When a membrane allows any true solution to go through including those solutions whose solutes are adsorbed negatively, then it is acting as a dialyzing membrane. It is understood, of course, that a solution which passes through by osmosis may under proper conditions—namely, after the membrane has coagulated—go through by diffusion or capillarity as through a dialyzing membrane. Calcium chloride does not necessarily fall out of the first class because even though both its ions are adsorbed equally, only at extremely low concentrations very dilute solutions will go through appreciably after a long enough time has elapsed without the membrane having been coagulated. And so sugar will go through copper ferrocyanide not because the latter is an ultrafilter, but because it has been converted into one through selective adsorption of cations and consequent coagulation. When a substance is brought in contact with a membrane in this condition and for which it possesses greater adsorption for the anion than for the cation the situation is reversed, the pores are closed because the copper ferrocyanide is peptized and it is no longer permeable to sugar. Such a membrane represents therefore a dynamic system. Its structure and its behavior must depend on the character of the substance which is trying to pass through. All this is very suggestive when we consider what takes place in the case of living cells.

---

[1] Z. physik. Chem. **10**, 699 (1892).

When Collander[1] contends that protoplasm probably acts as an ultra-filter toward substances which are not soluble in lipoids he does not apparently take into consideration the fact that cells are both permeable and impermeable for the same substance. In addition to this he assumes a sort of continuous lipoid film with holes in it. This is going beyond the facts known at present. Collander also takes it for granted that cells have present at all times on either side the membrane-forming reagents. No such simple assumption is adequate. It is not known how the membrane is formed. It may be kept intact by the constant accumulation on one side and dissipation on the other of substances which lower the surface tension of a liquid as they concentrate at the interface between the cell and the external medium; or by secretion or by a slow process of precipitation[2].

"A feature of the protoplasm of many cells is the existence of a more or less differentiated cortex. When the cortex is well differentiated, it is an appreciable zone of protoplasm which is more solid than the interior. This is specially well developed in many Protozoa. Paramoecium, for example, possesses a firm cortex, the ectoplasm, of a uniform thickness over the body of theorganism. It is a structural modification which cannot be easily, if at all, repaired by the more fluid endoplasm. In Paramoecium it is an elastic jelly-like wall which is under a certain tension due to internal turgor. This can be shown by tearing the ectoplasm with a micro needle. The fluid interior then pours out, while the torn edges of the ectoplasm curl in, and the entire animal shrinks in size. If the edges of the tear meet they unite and further outflow of the endoplasm ceases, otherwise all the endoplasm flows out and the ectoplasm soon disintegrates. The endoplasm as it pours out into the surrounding water occasionally forms a delicate surface film which maintains the integrity of the extruded mass. . Usually, however, the endoplasm becomes entirely dissipated and disintegrates. In some species, e.g. Paramoecium bursaria, the torn surface very readily forms a surface film which frequently persists. The integrity of the cell is thereby maintained. In the few experiments that have been made on this form, the endoplasmic surface film is apparently unable to regenerate a differentiated ectoplasmic layer. Complete recovery occurs by a gradual contraction of the animal until the ectoplasmic edges bordering the ectoplasmic surface film, meet and unite". Again "The surface film of blood cells and of tissue cells isolated in blood plasma or serum is extremely susceptible to mechanical injury unless special precautions are taken to maintain conditions as normal as possible. The human red blood corpuscle furnishes an interesting example of a rapid breakdown of the surface film. When the surface film is punctured with a very fine glass micro needle the hemoglobin immediately diffuses out all over the cell and leaves behind a transparent glutinous mass which can be torn into strands".

---

[1] Kolloidchem. Beihefte, 20, 273 (1925).

[2] Chambers: "General Cytology", 254, 255, 257 (1924).

From what has just been said it is evident that living membranes are left pretty much to their own resources, as it were, to manifest their phenomena of semi-permeability. And, therefore, if the copper ferrocyanide membrane is to exhibit analogous properties it must be used so as to imitate most nearly the conditions imposed upon living membranes. The first of these conditions requires the absence of the membrane-forming reagents. This condition Collander did not fulfill in his experiments. In addition to this the statement that the living membrane is probably an ultra-filter needs further correction. Collander has not taken the trouble, apparently, to differentiate between a semi-permeable membrane and an ultra-filter. To be sure he is not the only one. An ultra-filter is something which has been taken more or less for granted, and as a result no really definite idea has been in vogue. Accordingly Bancroft[1] has formulated the definition that "an ultra-filter is essentially a porous membrane which will, by hypothesis, never become a semi-permeable membrane unless there is a strong negative adsorption—preferential adsorption of the solvent." "The conclusion that a substance which can be filtered out through an ultra-filter is in colloidal solution and not in true solution rests on the explicit assumption that any gas or vapor will go through any pore through which any other gas or vapor will go". According to this idea—with which, after all, Collander cannot be confronted—everything in the cell which is in solution will ooze out and everything which is in solution will go in. The composition of the inside of the cell, as far as solutes go, will be identical with that outside. This, of course, is impossible. The simple ultra-filter idea must be revised.

On the other hand coagulation of the membrane and a reversal of the same explain a great many things, even though the structural character of the membrane is still a puzzle. The objection to Overton's lipoid theory[2] was that water-soluble substances like sugar could not penetrate a lipoid membrane. If however we assume the presence of a granular lipoid membrane analogous to copper ferrocyanide, in other words with each solid fat particle, or group of particles, surrounded with an adsorbed film of water supported in a separate pellicle, which is known to be present, we have essentially the same sort of thing as the copper ferrocyanide membrane and there seems to be no reason why, should such a membrane exist actually, it should not exhibit coagulation changes when necessary and allow e.g. sugar to enter the cell at one time and not at another. We have still to account however for the entrance of lipoid solvents through such a membrane. This is not at all a hopeless endeavor. Mention was made above of a film of adsorbed water surrounding the lipoid particles. It need not be that necessarily. The film could be a solution possessing properties analogous to a pyridine solution. In other words it might dissolve substances other than and in addition to lipoid solvents. In this way the lipoid particles would be available as carriers for substances like ether and chloroform. Such a membrane would have the advantage of manifesting osmotic pressure, unlike an emulsion, and also to exhibit permeability changes in localized areas of the cell surface. It must be understood that only a very generalized picture of cell membrane is attempted. Undoubtedly membranes must differ with the functions of the particular organs of which they form a part. It may be objected that a substance like pyridine which may dissolve lipoid solvents may also dissolve the lipoid portion of the membrane and so destroy it. This need not follow at all. Pyridine itself is soluble in rubber, but it has been used with rubber membranes successfully by Kahlenberg without the rubber being damaged even in boiling pyridine. On the other hand if the idea of a discontinuous membrane—that is a fine grained one—with adsorbed water around the particles is not an attractive one we can postulate the existence of a continuous lipoid film of some sort which acts ordinarily as a semi-permeable membrane allowing only such things to go through which dissolve in it. A change in the surface tension of the surrounding medium might coagulate such a membrane into solid or semi-solid drops and allow water-soluble substances to pass through. Such a membrane could be reversed by changing the surface tension of the surrounding medium perhaps in addition to the extraction of the coagulating agent from between the particles by the presence of a suitable solvent or reagent. The coagulating agent might be a water soluble soap resulting from the reaction between sodium chloride and some fatty compound. This soap would reduce the surface tension of the solid film and pores would be formed between the solid drops in the membrane. The presence of calcium chloride would form a water-insoluble inert calcium soap which would dissolve in the membrane and subsequently would be decomposed by the cell after an increase in the surface tension of the external medium reversed the membrane and made it once more continuous. Clowes was not far away from such an explanation but he insisted that the cell must be an emulsion.

---

[1] J. Phys. Chem. **29**, 966 (1925).

[2] Jahrbuch wiss. Botanik, **34**, 669 (1899).

For the membrane suggested at first, antagonism can exist between the substances which will tend to coagulate the membrane and those which will peptize it. In the case of copper ferrocyanide the antagonism established was between alcohol or an inorganic salt on the one hand and copper sulphate on the other. There are undoubtedly other substances besides copper sulphate which will accomplish the same thing. The object of the investigation was not so much to find what would peptize the coagulated membrane as to make sure that the re-peptization could be accomplished at all. The exact character of such antagonism as sodium-calcium must be left for future investigation when a membrane more nearly akin to a living one will be made.

We know that after death the cell membrane behaves as ordinary dialyzer. The phenomenon is probably a question of permanent and irreversible coagulation. Experiments with acetic acid suggest the cause to be increased acidity of living cells after death owing to the accumulation of lactic acid.

There is no doubt that coagulation and reversibility of cell membranes suggest an interesting line of attack for many a problem in physiology and pathology. Whether the analogy, which has been drawn, in this series of investigations, between an artificial membrane and ectoplasm is warranted time alone will tell.

Summary

1. Copper ferrocyanide membranes are coagulated by low concentrations of methyl alcohol, acetic acid, sodium chloride, potassium chloride and calcium chloride, thereby becoming permeable to sugar.

2. A copper ferrocyanide sol is flocculated by aqueous alcohol, whereas alkalies and water peptize a copper ferrocyanide gel.

3. The coagulation of copper ferrocyanide is caused by selective adsorption rather than by decrease in surface tension.

4. Copper ferrocyanide forms a granular membrane between those particles adsorbed water is present which fills the spaces more or less completely.

5. Copper ferrocyanide membranes are coagulated by water at a temperature of about 24°C.

6. The coagulation of copper ferrocyanide is reversible.

7. Bartlow's experiments with alcohol, Walden's experiments with acids, and Czapek's experiments with alcohols and acids involved nothing more mysterious than a coagulation of the membrane.

8. Intermittent permeability in living membranes is probably also a question of reversible coagulation.

This problem was suggested by Professor W. D. Bancroft to whom the writer is greatly indebted for invaluable criticism and suggestions.

Cornell University.

CATALYTIC ACTIVATION OF TITANIA

BY W. A. RUDISILL AND CARL J. ENGELDER

It is a well known fact that the activity of a catalyst is to a large extent dependent on its manner of preparation. The nature of the starting material and its subsequent chemical and physical treatment are factors in the preparation of a catalyst which have received scant attention by investigators. Adkins[1] and his co-workers have done some excellent work on selective activation. A recent article by Adkins and Bischoff[2] on the selective activation of titania catalysts points out how the activity of titania may vary with different titanium compounds as the starting material.

In the present investigation, a study has been made of some of the factors which influence the activity of titania catalysts in decomposing ethyl alcohol. As shown in the experimental results, the treatment given the catalysts during their preparation affects to a large degree the extent of the decomposition as well as the composition of the gaseous products. The decomposition of ethyl alcohol by various catalysts has been rather thoroughly investigated by Grigoreff[3], Ipatief[4], Sabatier and his colleagues[5], Engelder[6], Adkins and others. Oxide catalysts like TiO_2, SiO_2, and ZrO_2 possess the ability to decompose C_2H_5OH according to the two main reactions:

$$(1)\quad C_2H_5OH \longrightarrow H_2 + C_2H_4O$$
$$(2)\quad C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

the one a dehydrogenation and the other a dehydration, both proceeding simultaneously to an extent dependent upon the specific nature of the catalyst. Titania catalysts in particular differ widely in their specificity towards these two reactions. That this specificity is dependent, to a considerable extent, on the physical factors involved in the catalyst's preparation has been the object of this research.

The factors which have been studied here are as follows:—

1. Variation of the Temperature of Ignition of the Catalyst.
2. Variation of the Time of Ignition of the Catalyst.
3. Variation of Anion.
4. Variation of Degree of Fineness of Catalyst.

Experimental

Apparatus and General Plan.—The general mode of procedure was to pass the vapors of ethyl alcohol at a uniform rate over the catalyst mass contained in the decomposition apparatus and to collect and measure the gas volume evolved and determine its composition. The apparatus was similar to that used by Engelder with certain modifications suggested by Adkins and Nissen[1]. The alcohol was accurately measured and controlled by allowing mercury to fall into a burette from which the alcohol was displaced. It passed first through a preheater and then into the reaction tube of Pyrex glass. The catalyst was placed in a porcelain boat in the center of the tube. This reaction tube was maintained at a constant temperature of 350° by being surrounded by an electrically heated furnace, the temperature of which was controlled by a Leeds and Northrup thermo-regulator. The reaction products passed through a spiral condenser and then into an ice-cooled receiver, to collect the liquid products, the gases passing on into a large collecting bottle containing saturated salt solution, which served as a gasometer. Provision was made for sampling the gases from the gasometer, as well as from a sampling cock on the line leading to the collecting bottle.

---

[1] J. Am. Chem. Soc. 44, 2175 (1922).

[2] J. Am. Chem. Soc. 47, 807 (1925).

[3] J. Russ. Phys. Chem. Soc. 33, 173 (1901).

[4] Ber. 34, 596 (1901); 35, 1047, (1902); 36, 1990 (1903).

[5] "Catalysis in Organic Chemistry."

[6] J. Phys. Chem. 21, 679 (1917).

Gas Analysis.—The gas mixture was analyzed according to the usual methods of gas analysis. In some cases hydrogen was determined by the fractional method over spongy palladium as well as the regular slow combustion method over mercury. Ethylene was adsorbed in bromine water, CO_2 in KOH solution and CO in acid Cu_2Cl_2 solution. All gas volumes were recalculated to N.T.P. and reported as such.

Uniform Procedure.—After considerable preliminary work in which the apparatus was perfected, the technique standardized, and a score or so of weakly active catalysts were made and tested, the following uniform procedure for catalyst testing was adopted:—

All catalyst samples were ground to pass a 100-mesh sieve (except those whose degree of fineness was being studied). In each run 2.5 grams of the heated catalyst was used. The temperature for all runs with alcohol was 350°C. Absolute ethyl alcohol was used. The preheater was maintained at about 170°C. and the alcohol admitted at a uniform rate of 6 cc per hour. Readings of burette, temperature of preheater and reaction tube, and volume of gas were recorded at intervals of 3 to 5 minutes and slight adjustments made in the rate of flow whenever necessary. Alcohol was passed through the apparatus under the above conditions for one hour to free the train from air. At the end of the first hour the collected gas was discarded, and the run continued for another hour. The volumes of gas recorded and their composition are for the second hour.

1. Variation of Temperature of Ignition of Catalyst

Preparation of Catalysts.—Preliminary work indicated that the temperature to which the catalyst is subjected during its preparation is an important factor in determining its specificity. Accordingly two series of titania catalysts were prepared, starting with titanium potassium oxalate, kindly furnished us through the courtesy of the Lindsay Light Co., Chicago, Ill.

---

[1] J. Am. Chem. Soc. **46**, 140 (1924).

Catalysts designated by G.—The "G" series was made as follows: Titanium potassium oxalate was dissolved in water and precipitated with ammonium hydroxide. The precipitate was washed four times by decantation, filtered, and then washed on the filter. The precipitate was dissolved in dilute HCl and reprecipitated with NH_4OH. It was then washed again as described above. The precipitate was dried at 150°C. and then heated at the same temperature for three hours. It was then ground to pass a 100-mesh sieve. Separate portions of this were heated for periods of two hours each at temperatures of 300°, 350°, 450°, 550°, 650°, and 750°C., giving respectively catalysts G^1, G^2, G^3, G^4, G^5, and G^6. A portion of the 100-mesh, dried batch was reserved for later work.

Catalysts designated by H.—The "H" series was prepared in the same way, with the exception that the first precipitate of $Ti(OH)_4$ was redissolved in dilute H_2SO_4 instead of dilute HCl. Separate portions of the dried, 100-mesh batch were heated for two hours each at temperatures of 250°, 300°, 350°, 450°, 550°, and 650°C, giving respectively the catalysts H^0, H^1, H^2, H^3, H^4, and H^5. Other portions of this preparation were reserved for later work.

The activity of these "G" and "H" samples was then determined in the uniform manner adopted. The results are tabulated below in Table I.

The results clearly show the importance of proper temperature of drying the catalyst. With increasing temperature of ignition, for both series, beyond 350°C the total gas evolution falls off rapidly, and there is a corresponding decrease in the volume of C_2H_4 per cc. of alcohol, particularly with the "H" series. In general the "H" series of titanias is more active, especially in regard to dehydration (ethylene production). The best catalyst is that precipitated from the sulfate solution and ignited at 300°C. Quite apparently, changes have been brought about by the higher temperatures of ignition modifying the surface conditions, especially as regards the dehydration ability of the catalyst.

Small amounts of carbon dioxide and carbon monoxide were always found, doubtless arising from secondary decomposition.

Considerable amounts of ethane were always present, amounting to 23.8% in the case of the "H" catalyst ignited to 650°. The particular mechanism by which this is formed has not been definitely determined. Adkins[1] believes that the ethane is produced probably according to the reaction:

$$2CH_3CH_2OH \longrightarrow CH_3CH_3 + CH_3CHO + H_2O$$

one molecule of the alcohol being reduced to the saturated hydrocarbon, the other oxidized to acetaldehyde. It is possible, on the other hand, to assume hydrogenation of the ethylene, yet no evidence here or in previous work is available to substantiate this.

2. Variation in Time of Ignition of Catalyst

To determine whether the length of time of igniting the catalyst is an important factor, two series of runs were made with portions of the "G" and "H" lots reserved for this purpose. Separate portions of the reserve supply

---

[1] J. Am. Chem. Soc. **47**, 807 (1925).

TABLE I

All runs made at 350°C at the constant rate of 6 cc. alcohol per hour, with 2.5 grams of catalyst. Time of ignition, two hours.

Catalyst	Pptd from	Temp of Ignition	Gas Envolved per cc. Alcohol 2d hr.	Composition of Gas Mixture. % C_2H_4	% H_2	% C_2H_6	% CO	% CO_2	cc. H_2 per cc. alcohol	cc. C_2H_4 per cc. alcohol
G^1	Chloride Solution	300°	85	46.4	38.7	14.6	0.9	0.5	31.9	39.4
G^2	" "	350°	92	48.9	29.8	18.3	0.7	1.1	27.4	45.0
G^3	" "	450°	78	47.7	35.2	16.0	0.8	1.2	27.4	37.2
G^4	" "	550°	60	41.8	41.8	15.6	0.7	1.0	25.1	25.1
G^5	" "	650°	34	24.8	62.7	11.1	0.5	0.7	21.1	8.4
G^6	" "	750°	16	7.5	82.7	7.5	0.7	0.7	13.2	12.0
H^0	Sulfate Solution	250°	113	71.4	7.2	20.4	0.8	0.8	15.8	80.8
H^1	" "	300°	140	67.8	7.7	22.8	1.2	1.4	10.7	94.9
H^2	" "	350°	93	73.3	8.5	17.1	0.8	0.7	8.4	72.5
H^3	" "	450°	95	71.4	9.2	18.1	0.9	1.2	8.7	67.8
H^4	" "	550°	74	63.4	15.8	20.1	0.8	1.0	11.7	46.9
H^5	" "	650°	35	51.1	24.2	23.8	0.6	0.3	8.4	17.8

were heated, at 350°C. for 1, 4, and 6 hours giving respectively the samples designated as H^6, H^7, H^8, and runs made under identical conditions as with H^2. A similar series was made with the "G" lot precipitated from chloride solution. The results for one set are here reported.

TABLE II

All runs made at 350°C. at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst, precipitated from sulfate solution.

Catalyst	Time of Ignition	Gas evolved per cc. alcohol		% H_2	% C_2H_4	% C_2H_6	% CO	% CO_2
		1st hr.	2d hr.					
H^6	1 hr	105	98	7.9	74.9	16.1	0.9	0.8
H^2	2 "	112	99	8.5	73.3	17.1	0.8	0.7
H^7	4 "	95	90	8.4	74.8	15.3	0.7	0.8
H^8	6 "	150	91	6.9	68.3	21.8	1.0	1.3

The results show that the time factor of ignition is of little importance, the yield of gas being almost the same after the first hour and its composition practically the same for the several catalysts. Somewhat lower yields were obtained with the corresponding "G" catalysts, but they were practically constant both as regards total volume and percentage composition.

3. Influence of Anion

The series of experiments recorded in Table I indicated that the catalysts made by reprecipitation from a sulfate solution gave in general a more active catalyst than that series prepared by reprecipitation from a chloride solution. Both series otherwise received the identical treatment, such as uniformity in concentration, quantity of wash water, etc. The observed differences in behavior might be ascribed to the influence of the anion in the solution from which precipitation was made, or to adsorbed anions. To obtain further data on this point, some additional catalysts were prepared and two series of runs on alcohol made.

The catalysts designated as "J" were prepared in the same way as the "H" series except that the final precipitate was purposely not washed free from sulfate. One portion, J^1, was heated to 300°C and the second portion, J^2, to 350°C. These unwashed samples were compared in their effect on alcohol at 350°C. with the thoroughly washed samples, H^1 and H^2.

Catalysts "K" were made by dissolving potassium titanium oxalate in water and precipitating by ammonium hydroxide. The precipitate was washed four times by decantation, filtered and then washed on the filter. Up to this point, the treatment was identical as that given to the lot from which the "G" and "H" series were derived. The mass was then dried at 150°C for three hours. One portion was heated for two hours at 300°C, giving K^1; another portion was heated to 350°C for two hours, giving K^2. Runs were made with alcohol at 350°C by the standard procedure.

Still another series of catalysts was made by precipitating the hydroxide, filtering, dissolving in hydrochloric acid and then largely diluting and precipitating the $Ti(OH)_4$ by boiling. The hydrolyzed precipitate was washed, dried, heated to 150°C for three hours and separate portions, passing a 100-mesh sieve, were heated to 300°C and 350°C, giving respectively the catalysts designated as L^1 and L^2.

The tabulated results are given in the table below.

TABLE III

All runs made at 350°C at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst. Time of ignition two hours.

Catalyst	Method of Preparation	Temp. of Ignition	Gas evolved per cc. Alcohol		Composition of Gas Mixture				
			1st hr.	2d hr.	% C_2H_4	% H_2	% C_2H_6	% CO	% CO_2
H^1	Sulfate-Washed	300°	150	140	67.8	7.7	22.8	1.2	1.4
J^1	Sulfate not washed	300°	155	84	69.7	4.8	23.8	0.9	1.1
K^1	Oxalate	300°	84	27	40.9	20.6	35.7	1.4	1.1
G^1	Chloride	300°	104	85	46.4	38.7	14.6	0.9	0.5
L^1	Hydrolysis of Chloride	300°	117	103	76.0	4.6	18.0	0.4	1.5
H^2	Sulfate Washed	350°	112	99	73.3	8.5	17.1	0.8	0.7
J^2	Sulfate not washed	350°	150	81	66.0	3.1	29.1	0.9	1.0
K^2	Oxalate	350°	89	25	31.0	27.9	36.9	0.9	3.0
G^2	Chloride	350°	111	92	48.9	29.8	18.3	0.7	1.1
L^2	Hydrolysis of Chloride	350°	139	128	70.8	4.7	22.9	1.0	1.1

That thorough washing is necessary to give an active catalyst and one that does not depreciate with prolonged use is shown by a comparison of H^1 with J^1 and H^2 with J^2. The unwashed samples rapidly lost their activity.

Reprecipitation is very important, as shown by the runs with the samples prepared from the oxalate without reprecipitation. A rather inactive catalyst, particularly in its dehydrating ability results from only one precipitation. The unusually high values of ethane are significant.

Preparation of samples by hydrolysis yields a very active catalyst. This bears out the results of other investigators who have found that in general hydrolytically prepared catalysts are very efficient.

4. Variation in Degree of Fineness

It is to be expected that for the same weight of catalyst, the finer particle size and hence the more surface exposed, the greater will be the activity, other conditions being the same. Since titania influences both decomposition reactions of ethyl alcohol, it was thought interesting to study the variation of particle size with the extent to which these simultaneous reactions are effected. Accordingly, a series of samples was prepared as follows:—The method of preparation of the "G" catalysts was followed closely. The lot dried at 150° for three hours was divided. One portion was ground to pass a 20-mesh sieve, but withheld by a 40-mesh sieve; this is designated as M^1. Another portion was ground to pass a 100-mesh sieve; this is called M^2. A third portion passed a 200-mesh sieve; this is M^3. Each portion was then heated for two hours at 350°C.

Runs by the uniform procedure were then made with alcohol, using as always, 2.5 grams of the catalyst. The data are given in Table IV.

TABLE IV

All runs made at 350° at the constant rate of 6 cc. alcohol per hour with 2.5 grams of catalyst.

Catalyst	Temp. of Ignition	Time of Ignition	Gas per cc. alcohol		Composition of Gas Mixture					cc. C_2H_4 per cc. alcohol.	cc. H_2 per cc. alcohol.
			1st hr.	2d hr.	% C_2H_4	% H_2	% C_2H_6	% CO	% CO_2		
20-40 mesh (M^1)	350°	2 hrs.	106	91	49.2	34.0	15.1	0.8	1.0	44.6	30.9
100-mesh (M^2)	350°	2 "	120	95	50.0	29.5	18.4	1.5	1.3	47.5	28.0
200-mesh (M^3)	350°	2 "	130	115	51.5	25.2	20.9	1.3	1.3	59.2	28.9

An increase in activity is shown for an increase in the degree of subdivision. More interesting, however, is the increase in dehydration with the finer sized contact masses, as indicated in the increased amounts of ethylene obtained. An increase in the amounts of ethane is also observed. Degree of fineness is thus another factor influencing the specificity of catalysts.

5. Stability of Catalyst

The relative stability of the different catalysts used is indicated by a comparison of the volume of gas during the first and second hours. Of the many catalysts prepared and studied in this investigation the ones designated as H^1 and L^2 were the most active. In order to determine the life of the catalyst, i.e., its activity with prolonged use, a catalyst was made according to the H series with a preliminary ignition of two hours at 300°C., giving catalyst H^9, and subjected to a ten-hour run. The results of this run are given in Table V.

Samples of the gas were analyzed at the end of the second, fourth, seventh and tenth hours. Catalyst H^9 depreciated very slowly with continued use and the composition of the gas after the first three hours changed very little. There was a slight increase in ethylene and in ethane between the second and fourth hours. The percentage of hydrogen was low and showed very little change.

TABLE V

Time		Gas Envolved per cc. Alcohol	% C_2H_4	% H_2	% C_2H_6	% CO	% CO_2
1st	Hr.	154	—	—	—	—	—
2d	"	139	69.2	6.9	22.3	0.9	1.3
3d	"	132	—	—	—	—	—
4th	"	136	66.2	3.9	25.9	1.1	1.4
5th	"	135	—	—	—	—	—
6th	"	126	—	—	—	—	—
7th	"	128	66.2	4.6	26.5	1.2	1.4
8th	"	120	—	—	—	—	—
9th	"	122	—	—	—	—	—
10th	"	118	66.9	5.4	26.8	1.4	1.0

Summary

1. Some of the factors which influence the activity of a catalyst have been studied in detail by preparing a large number of titania catalysts, passing the vapors of ethyl alcohol over them at a temperature of 350°C., and noting the volume of gas produced as well as its composition.

2. It was found in the first place, that the temperature of ignition of the catalyst greatly influenced both the yield of gas and its composition. In general, it was found that with increase in temperature of ignition there was a decrease in activity, and further, a decided decrease in ethylene production. In order to produce a good dehydrating catalyst the temperature must be low.

3. The preliminary ignition period of two hours is sufficient for the preparation of an efficient catalyst. Heating beyond one hour has little effect.

4. It was found that the character of the anion present during precipitation is important. Those catalysts made by precipitating from sulfate and chloride solutions and by hydrolysis were the most efficient. Those prepared from the sulfate and by hydrolysis gave the highest percentage of ethylene and the lowest percentage of hydrogen. Catalysts prepared by precipitation from the oxalate gave the lowest activity, the lowest percentage of ethylene, and the highest percentage of ethane. Catalysts prepared from thoroughly washed precipitates were the more active.

5. The degree of fineness of a catalyst influenced to some extent its activity. As the degree of fineness was increased, the activity was increased. Grinding the catalyst to fine mass before final ignition gave a more active catalyst.

6. Some catalysts were prepared which depreciated very slowly with use. A catalyst prepared from the sulfate solution was very active after ten hours use.

University of Pittsburgh,
Pittsburgh, Pa.
Oct. 1925.

FILMS OF ADHESIVES*

BY J. W. MCBAIN AND D. G. HOPKINS

Our previous work[1] has divided joints into two classes, specific and mechanical. Joints between smooth surfaces are necessarily specific, that is, true adhesion must occur between the surfaces and the film of adhesive. We have noticed that the strength of such joints is parallel to the mechanical constants of the materials joined and the question immediately arises as to whether there should not be a similar definite relation between their strength and the mechanical properties of the film of adhesive itself.

The second class of joints has a purely mechanical explanation in that the adhesive is embedded in the pores and surface irregularities of the materials joined. Here the film of adhesive acts as a solidified casting holding the materials together. Glued wooden joints appear to be a conspicuous example of this class. It is evident that for any given material the strength of such a joint must depend upon the mechanical properties of the film of adhesive, its penetrating power in the liquified state, its rigidity and tensile strength and absence of brittleness in the solidified state. For both classes of joint the tensile strength of the film itself imposes an upper limit on the strength of joint obtainable, since the film in both cases must transmit the strain.

Thus an investigation of adhesive action necessarily involves a study of the properties of adhesive films. Even as a routine test the study of a film of the adhesive itself should give more direct information than could be obtained in any other way.

The difficulty in the way of most investigators has been to procure suitable test specimens of the dried adhesive, and has been overcome only in a very few instances by following an elaborate and troublesome procedure[2]. We find that it is possible to employ a very rapid and simple method by adopting

---

*This investigation was undertaken for the Adhesives Research Committee of the Department of Scientific and Industrial Research and the authors are indebted to the Department for permission to publish the results.

[1] Table III of the previous paper (J. Phys. Chem., 29, 195 (1925); see also Second Report of Adhesives Research Committee, 1925) should have been completed by the insertion of the following particulars with regard to the various grades of silicate of soda employed.

Grade	ρ = (density of solutions)	% Na_2O	% SiO_2
D	1.70	18.5	36.0
K	1.56	13.8	32.9
C	1.50	11.65	32.85
J	1.375	9.06	26.44
A	1.39	9.14	29.36
Experimental sample	1.225	4.94	19.53

In footnote (***) of the same table the statement "three coatings instead of one raised the strength of joint with starch to 1600 lbs" should be amplified by pointing out that this special result was obtained with a double-cover plate type test piece, where the total load is given and not the strength in lbs per sq. in. The corresponding value for a high-grade glue is about 3000 lbs total load.

[2] Thus Hopp (J. Ind. Eng. Chem., 12, 365 (1920)) and Gill (17, 297 (1925)) both obtained values of 12,000 to 13,000 lbs. per sq. in. for a high grade glue.

the device of using very thin films, which can be tested with an accuracy far surpassing that of any known wooden join.

Furthermore, the strength of such films is far greater than that of any wooden join and is equaled only by the end grain strength of the strongest woods. Up to the present no really satisfactory type of wood joint has been evolved, either as regards of accuracy of measurement or absolute strength as compared with the glue itself. It appears that a glue may be appreciably deteriorated before there is any falling off observable in the strength of joins made there from, probably because the strength of the joins is such a small fraction of that of the glue itself. These thin films also allow a ready method of investigating not only the tensile strength but also such important mechanical properties as rigidity and brittleness and the limit of deformability.

The necessity for study of the film cannot be obviated by merely studying the properties of the liquid or dissolved adhesive such as jelly strength, viscosity etc., although this is commonly assumed in the case of glue. On the other hand, the writers are well aware that tensile strength, although an essential factor, is only one of the many mechanical properties of the film itself which have to be considered. Further, there are other important qualities which must be possessed by the solution (prior to the formation of the film) such as penetralibility, rate of setting etc.

Paper Strip Method

Before describing our work with thin films some data may be given which show that the method of using strips of paper impregnated with glue[1] cannot be considered satisfactory, although it has recently been advocated by Bechhold.

This method is incapable of giving an absolute measure of the strength of adhesive films because the true cross-sectional area of the film cannot be determined even approximately, and further the effect of the presence of the paper cannot be gauged, nor the effect of the adhesive upon the paper itself. The method is limited to obtaining the order of magnitude of the tensile strength.

A slight modification of Millar's method was adopted in the following experiments carried out to investigate the possibilities of the method. Pure cellulose paper was cut into dumb-bell shaped strips 5″ long and 1″ wide in the narrow part. These test pieces were dipped into the adhesive solution and then hung up by the end to dry. When dry the process was repeated but this time they were allowed to dry in the reverse position so that a fairly uniform coating of adhesive was obtained. Tension tests were then carried out, the breaking loads being measured to the nearest pound and the mean of four determinations taken. The thickness of the strip at the point of fracture was determined in six places with a micrometer reading to 0.001″. Table I gives the order of magnitude of the tensile strengths of a number of adhesive films, made from aqueous solutions.

---

[1] Millar: J. Soc. Chem. Ind., **18**, 16 (1899).

TABLE I

Tensile strength of films of adhesive made from aqueous solutions.

Strip	Concn. %	Heated to (°C)	Thickness of strip (10^{-3}in)	Total breaking load (lbs)	Net* breaking load (lbs)	Tensile** strength (lbs/sq. in.)
Paper only	—	—	3	7	0	(2000)
Paper + adhesive H***	10	60	4	36	29	7000
Paper + gelatine X***	10	60	5	41	34	7000
Paper + starch	2	60	4	14	7	2000
Paper + gum arabic	10	18	4	15	8	2000
Paper + silicate†		18	7	16	9	1000

*Breaking load for impregnated strip less breaking load (7 lbs) for paper.
**Order of magnitude only = adhesive − paper.
***See p. 119 for information regarding these adhesives.
†Molar ratio 3.0, density 1.375

It is evident from these results that the paper strip method is not satisfactory for comparing the tensile strengths of different adhesives. Not only has the paper itself an unknown influence upon the structure and mode of fracture of the film but its own strength is too large a fraction of that of the film to allow the data to possess any quantitative significance. Some of these adhesives are many times stronger than would here be indicated.

The preparation of test pieces of adhesive film.

The most trustworthy method of testing the strength of films of adhesive is by measuring the strength of thin films which have been formed by allowing them to dry on a surface to which they will not adhere. The thinnest films obtainable should be used in order to minimise strains which may develop in drying. Such films also approach most nearly to the condition of the adhesive in a joint.

This simple method of procedure has been adopted by which thin films may be readily prepared and tested. The results are sufficiently concordant to warrant the assertion that this method will supplement and to some extent supersede those which are at present in use. It also affords a ready means of investigating the effect of addition of soluble substances, or powders (fillers) upon the strength of glue and gelatine films. This method has already supplied new and highly significant information.

Farrow and Swan[1], using a suggestion of J. H. Sturgess, prepared thin films of starch by pouring starch solutions on to very thinly greased ferrotype plates, where they were allowed to dry. The films were readily detachable from the plates. Neale[2] has thus found that such starch films possess considerable tensile strength (2½ to 4½ tons per square inch).

Glue or gelatine was soaked in the requisite amount of water overnight and a solution prepared by heating at about 60°C. This solution was poured on to ferrotype plate coated with a trace of vaseline. On drying, which usually takes a few days, the film very frequently separated spontaneously from the greased surface but if it had adhered it could be removed by upraising the edges with a knife. A few films (e.g. gelatine with added phenol, chloral hydrate, sodium fluoride or sodium iodide) adhered strongly to the greased plate and it was not possible to detach them in portions large enough for the making of test pieces. Celluloid was occasionally used in place of the ferrotype plate although it showed a tendency to warp.

---

[1] J. Textile Inst. 14, T465 (1923).

[2] J. Textile Inst. 15, No. 9.

Films of gum arabic are particularly interesting because as they dried they became so brittle that they spontaneously broke into small pieces from internal strain. They could be rendered soft and flexible by slightly humidifying them but were as brittle as ever when dried again. It is possibly for this reason that glycerine is frequently recommended as an addition to gum arabic adhesives and indeed small quantities of non-volatile solvents are added to most adhesive compositions.

Care has to be taken in order to obtain really good films. One of the principal difficulties to be overcome is the elimination of air bubbles, for fractures originate at such points. In order to get a perfectly homogeneous adhesive solution it is necessary to shake or stir very thoroughly. Each of these operations has a pronounced tendency to produce air bubbles which are extremely difficult to get rid of on account of their great stability. In practice it has been found most satisfactory to give a whirling motion to the solution. When solids are added to the adhesive solutions the difficulty is still further increased because the powdered materials themselves enclose considerable quantities of air. The powder also tends to separate out both in the vessel from which the suspension is poured and on the ferrotype plate. Particles of certain substances, such as barium sulphate, agglomerated in glue and gelatine solutions.

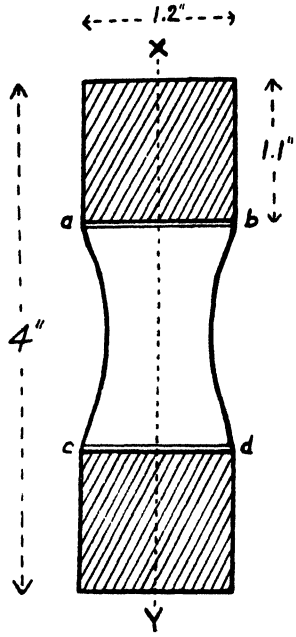


Fig. 1

When studying the effect of the addition of soluble substances it is necessary to make the addition in such a way that the resulting solution is quite homogeneous. For instance, alum could not be satisfactorily dissolved in a 10% gelatine solution. It was found better to soak the gelatine in the alum solution. On the other hand, formalin could not be added to the water in contact with the gelatine as it rendered the latter insoluble; it was added to the warm gelatine solution.

When finally prepared the film was slightly rehumidified to prevent it from splitting and then cut with scissors into test pieces, two types of which have been employed. The first or earlier type is shown in Fig. 1. Parallel lines ab and cd are drawn lightly in black lead at right angles to the central axis XY so as to facilitate fixing in the testing grips in such a way that the load is applied axially. The two wide end portions are reinforced with stiff paper so that a satisfactory grip can be secured in testing. This type of test piece may perhaps be criticised on the ground that it is easy to initiate a rupture when forming the curved edges by cutting with scissors. To obviate this the second and final type of test piece was designed (Fig. 2). It consisted of a straight strip the long sides of which could be cut out with one stroke of the scissors. The ends were reinforced with stiff paper as before, the paper being pressed on to the wetted adhesive strip. The results obtained with the two different forms of test piece were practically identical but the second type is to be prefered on account of its simplicity and from the point of view of economy of material.

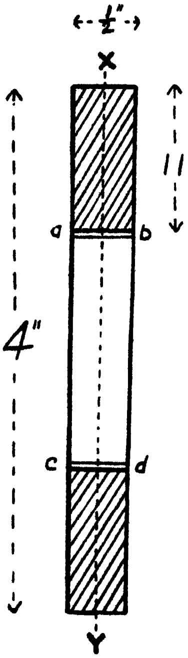


FIG. 2

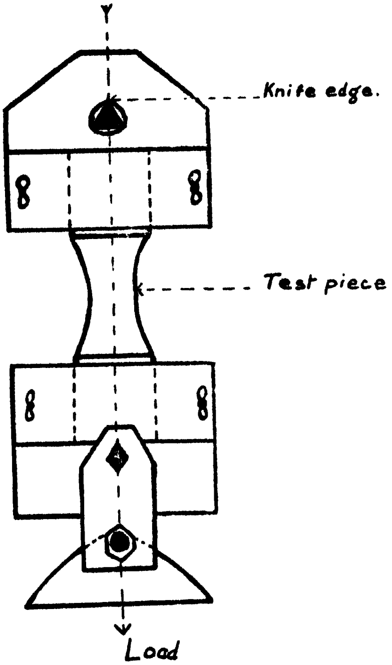


FIG. 3

The tensile strength of glue and gelatine films is greatly influenced by the hygrometric state of the atmosphere in which the tests are made. However, the variation of humidity in a room maintained at approximately the same temperature and otherwise under the same general conditions is often so small that it can be ignored in the case of most films. When certain soluble substances are added to the glue however, it becomes necessary to take the humidity factor into account and for accurate determinations, absolute or relative, it was necessary to carry out the experiments in an atmosphere of constant humidity. The humidity of the testing room was recorded in all later experiments being measured by means of a hair hygrometer.

The pattern of the grips employed is indicated in Fig. 3. The whole system was supported on a horizontal knife edge and the load applied by placing weights and sand in a bucket suspended from the lower grip, the rate of loading being maintained constant as far as possible.

In the majority of films the mean thickness may be taken in calculating the cross sectional area but in those cases where the film was not of uniform thickness the mean of six readings, three on each side of the point of fracture has been used in calculating the tensile strength. All measurements were made with a micrometer gauge reading to a ten thousandth of an inch.

Particulars of the solutions from which the films have been prepared are given in Tables II-IV. A few notes are however necessary to indicate the nature of the adhesives employed which appear in the tables under arbitrary designations.

(*a*) *Gelatine and glue* (without additions)
Gelatine X—a high grade commercial gelatine.
Highly purified gelatine—supplied by Prof. Schryver.
Isinglass—refined.
Adhesive H—a high-grade commercial glue.
Glue size—a proprietary brand.

(*b*) *Glue with added solids* (powders).
Lead sulphate—ordinary quality.
Zinc oxide—Kahlbaum's heavy.
Aloxite—finely ground
Fine water ground flint (fired) } supplied by Sir Herbert Jackson.

(*c*) *Glue or gelatine with added soluble substances*
Potassium dichromate—the films were exposed to diffused sunlight for seven days.
Formalin
Potassium alum } —these substances increase the viscosity of glue and gelatine solutions.
Sodium benzoate—this salt lowers the jelly strength.
Sodium formate
Sodium salicylate
Glucose } —these had been said to increase the adhesive power of the glue.

The effect of the prolonged heating of a glue solution on the tensile strength of the resulting films.

The loss of adhesive power of a glue solution by continued heating at various temperatures has already been followed by determining the strength of wood joints set up with the heated glue solutions[1]. It was pointed out that the wood joint method could be fully satisfactory for this purpose only in the case of adhesives which are less tenacious than the wood. In the present series of experiments the cause of the degradation has been followed by measurement of the tensile strength of the glue films.

---

[1] McBain and Hopkins: J. Phys. Chem. **29**, 203 (1925).

TABLE II

Glue and gelatine films (without additions)

Adhesive	Grams Adhesive in 100 gms water.	No. of determinations	Humidity %	Tensile strength			(lbs/sq. in.) Representative value.
				Maximum	Minimum	Mean	
Gelatine X	10	12	—	13300	10700	11900	12800
Highly purified gelatine	10	5	—	9800	9200	9500	9500
Isinglass (refined)	10	3	63	9900	9100	9500	9500
Adhesive H (1)	15	6	—	13000	10200	12100	12400
Adhesive H (2)	30	5	44	13400	12100	12200	12200
Glue size	50	2	53	7800	6600	7200	7200

TABLE II

Powdered solid added to 15 grams of adhesive H in 100 grams of water

Powder added	Wt. powder added (gms)	Added solid calculated on wt. of glue.	No. of determinations	Humidity %	Tensile strength			(lbs/sq. in.) Representative value.
					Maximum	Minimum	Mean	
Lead sulphate (1)	10	66⅔	5	61	8900	8200	8500	8500
Lead sulphate (2)	2.2	15	5	44	12400	11300	11900	11900
Lead sulphate (3)	1.5	10	5	44	12800	11200	11900	12300
Zinc oxide	10	66⅔	5	—	7800	5600	6700	7300
Aloxite	10	66⅔	3	—	6600	4900	5700	6100
Fine water ground flint (fired)	10	66⅔	5	—	6000	4300	5300	5700

TABLE IV

Glue (Adhesive H) and Gelatine X with added soluble substances

Substance	Films prepared from (gms.)			No. of detns.	Humidity %	Tensile strength			(lbs/sq. in.)
	Adhesive	Water	Substance			Maximum	Minimum	Mean	Representative value.
Films from glue (tensile strength without additions 12300 lbs/sq. in.)									
Formalin	15	100	5 (ccs)	4	52	13200	11300	12000	12700
Sodium benzoate (2)	30	100	3.0	4	44	12600	11300	11900	12300
Sodium formate (1)	15	100	2.0	6	52	7600	6200	6800	7100
Sodium formate (2)	15	50	2.0	5	44	7900	6600	7400	7900
Sodium formate (3)	10	30	0 20*	3	50	10500	9200	9800	9800
Sodium salicylate (1)	15	100	2.0	8	61	7300	4900	5900	5900
Sodium salicylate (2)	15	50	2.0	3	44	11000	9900	10500	10500
Sodium salicylate (3)	10	30	0.48*	4	50	9100	8900	9000	9000
Glucose (1)	15	100	5.0	6	54	3000	2500	2800	2900
Glucose (2)	15	50	5.0	6	44	6100	5400	5800	6000
Glucose (3)	10	30	0.59*	3	50	9000	8900	8900	8900
Hydrochloric acid	25	100 ccs N/10 soln.*		4	53	12900	11500	12200	12200
Sodium hydroxide	25	100 ccs N/10 soln.*		4	54	10000	9400	9700	9700
Films from gelatine X (tensile strength without addition 12800 lbs/sq. in.)									
Potassium dichromate	10	100	2.0	8	—	14100	11200	13200	13800
Potassium alum (1)	10	100	3.0	5	58	10800	8300	9400	9000
Potassium alum (2)	10	100	5.0	4	—	10800	8300	9400	10300
Sodium benzoate (1)	10	100	3.0	4	58	1500	1100	1300	1300

* = 0.1N solutions.

Ordinary aqueous as well as acid and alkaline solutions of glue have been experimented with, 25 grams of adhesive H being taken in 100 grams water or 100 grams of N/10 hydrochloric acid or N/10 sodium hydroxide. The solutions were prepared in the usual way and then transferred to sealed tubes or well-stoppered bottles and maintained at definite temperatures in thermostats. At intervals films were prepared and tested. An examination of the recorded humidities shows that it was possible to obtain satisfactory results without employing a constant humidity chamber by suitably choosing the times of testing.

No trouble was experienced in detaching films of acid glue from the greased ferrotype plate but those prepared from alkaline glue generally adhered quite firmly to the plate and in many instances it was impossible to detach them in a form suitable for testing. The results are given in Table VI.

TABLE VI

The effect of prolonged heating of a glue solution on the tensile strength of the films

	Temp. °C	Tensile strength (lbs/sq. in.) after period of heating in days.						
		0	1	2	3	6	28	45
Aqueous solution of adhesive H(25%)	55-57.5[1]	12200	12500	11400	11100	12800	11300	7800*
			(53)	(53)	(53)	(44)	(50)	(51)
	80[1]	12200	11200	11100	9000*			
			(50)	(50)	(50)			
	90[1]	12200	9700	4300*				
			(51)	(54)				
	100[2]	12200	**	**	**			
	57.5[2]	12200	11200	10300	10400	9300	***	
			(53)	(53)	(53)	(44)		
	55[3]	9700	†	8600	†	†		
		(54)		(54)				

[1] Aqueous solution of adhesive H (25%).
[2] 0.1 H Cl solution of adhesive H (25%).
[3] 0.1 NaOH solution of adhesive H (25%).
*Only one value obtained. Films very brittle and broken in fixing in machine.
**All films brittle and broken in fixing in machine.
***Films fractired spontaneously on drying. No test pieces could be prepared.
†Film adhered to greased plate.

Films prepared from 25% solutions of glue in water or in 0.1N hydrochlorid acid were equally tenacious. When, however, the solvent was 0.1N sodium hydroxide a scum appeared on the surface and the films were decidedly weaker.

Films from 25% aqueous glue solution that had been maintained at 55-57.5°C showed a slight reduction in strength after 28 days but after 45 days the loss was quite marked. At 80°C there was a decrease of about 9% after 2 days whilst after 3 days the strength had fallen to three quarters of the original value. At 90° the loss of strength was much more rapid, the value being reduced to one-third of the original in two days. Bogue[1] investigated the effect of the prolonged heating of glue solutions at 80° on their adhesive power by carrying out shear tests with the adhesive between maple surfaces and the loss of strength appeared to amount of more than 5% of the original strength per hour of heating, or to 67% loss in 12 hours. Continued heating of a glue solution is known to reduce its covering capacity and it is possible that thinning of the glue accounts for the discrepancy between Bogue's results with wood joints and the more direct ones obtained by the film strength method.

---

[1] Chem. Met. Eng. 23, 201 (1920).

The rate of loss of tensile strength of films prepared from a 25% solution of glue in 0.1N hydrochlorid acid maintained at 57.5° is much greater than with the aqueous solution, presumably on account of increased hydrolysis. The effect of alkali on the strength of a glue film is appreciable even at a temperature of 55°, a reduction of 11% taking place after 48 hours of heating.

One of the most important observations arising from the present series of experiments is that hydrolytic deterioration of a glue is accompanied by increasing brittleness of the adhesive film, especially at higher temperatures. Many films of comparatively high tensile strength were found to be exceedingly brittle and this factor is of considerable importance in estimating the adhesive power of a glue.

Discussion

The extreme variation between maximum and minimum values of tensile strength found in repeated experiments with a given adhesive was well within 10% whereas it is well known that results with wooden joints fluctuate by 20 or 30% even with the most careful control.

Gill[1] has determined the tensile strength, joint strength, viscosity and jelly strength of glues from six different sources (bone, hide and fleshings etc.) and found that the strengths of all the glues, except junk bone, were approximately the same (10000-12000 lbs/sq. in.). The strength of his wood joints with the same glues varied only from 3085 to 3940 lbs/sq. in. Gill concluded that the uniformity of tensile strength excluded the test as a means of discriminating between glues. This deduction is hardly justified by his own results since with junk bone where the tensile strength is as low as 4500-6500 lbs/sq. in. the joint strength is reduced to 2635 lbs/sq. in. Reference to Table II shows that the tensile strength of a film of a high grade glue (adhesive H) is nearly twice that of one prepared from a sample of glue size which had been selected as an example of a poor glue. Incidentally it may be remarked that the results of Gill's investigations demonstrate the absence of any parallelism between the joint strength and jelly strength or viscosity

The tensile strengths of films of gelatine X and adhesive P indicate that at least for mechanical joints a high grade gelatine and a good glue are equally efficient. Refined isinglass and a highly purified gelatine were found to be of about the same tenacity but rather inferior to a first class commercial gelatine or glue.

---

[1] Ind. Eng. Chem. **17**, 297 (1925).

The gelatine, glue and isinglass films, when loaded to near the point of fracture, developed permanent opaque markings which suggested the existence of slip planes or crystallisation of the adhesive. This persisted after the withdrawal of the load. However, examination of one of these fractured films by X-rays (transmission and reflection) gave no indication of crystalline structure.

The fact that gelatine and glue possess a tensile strength of more than five tons per square inch shows that wood joints do not measure the strength of a high grade glue. Wood is incapable of withstanding such a stress except in tension perpendicular to the end grain.

From the results obtained with addition of lead sulphate (Table III) it is evident that the effect of the addition of a powdered solid to a glue solution on the strength of the resulting films depends upon the quantity added. The addition of 10–15% of lead sulphate, calculated on the weight of glue, does not appreciably affect the tensile strength of the film, whilst if the addition was increased to 66⅔% the film was weakened by 31%. With such heavy loading of the glue, zinc oxide, aloxite, and fine water-ground flint (fired) caused even greater weakening. Even so, however, a weakening might escape detection in the use of wooden test pieces. Indeed, in some cases if surfaces to be united do not come into close contact, an added powdered solid may even increase the strength of the joint by enabling the film of adhesive to remain sufficiently voluminous to fill the space between the rough surfaces.

Only one of the soluble substances added to the glue definitely increased the tenacity of the film; namely, potassium dichromate. Formalin left it unimpaired. Potassium alum in two different concentrations reduced the film strength but alum separated in solid form when the adhesive solution dried on the ferrotype plate and this might have been of some account in bringing about the observed decrease.

A 10% solution of gelatine prepared in a 3% aqueous solution of sodium benzoate produced films which when tested in an atmosphere of 58% humidity were of very low tenacity and which elongated even under small loads. With a 30% glue solution prepared in a 3% solution of the same salt the films were of normal strength (12300 lbs/sq. in.) but the humidity in this case was only 44%, a factor which may largely explain the difference in the two values. Sodium formate, sodium salicylate and glucose weakened glue films considerably and the results obtained likewise show the influence of humidity.

Summary

1. Determinations have been made of the tensile strengths of thin films of a high grade commercial glue and gelatine, highly purified gelatine, refined isinglass and glue size. The first two adhesives gave values of about 5½ tons per sq. in. or twice that obtained with glue size. Refined isinglass and the highly purified gelatine had approximately the same tenacity; namely, 9500 lbs/sq. in. The tensile strength depends upon the humidity of the atmosphere.

2. The addition of 10-15% of powdered lead sulphate did not affect the tensile strength of the film appreciably, although 66⅔% did. Similar results were obtained when the glue was loaded with zinc oxide, aloxite and fine water-ground flint.

3. The presence of potassium dichromate definitely increased the strength of the film whilst formalin had no effect. Potassium alum, sodium benzoate, sodium formate, sodium salicylate and glucose reduced the tensile strength. Films prepared from 25% solutions of glue in water or in n/10 hydrochloric acid were equally tenacious whereas films prepared from glue dissolved in N/10 sodium hydroxide were decidedly weaker.

4. The hydrolytic degradation of such aqueous, acid and alkaline solutions of glue continuously heated causes a relatively slight loss of tensile strength even after 28 days heating at 55-57.5°C but the effect is much greater at higher temperatures and the films even when of high tensile strength become extremely brittle.

5. The experimental error involved in determining the tensile strength of adhesive films by this method is generally much less than 10%. The results appear to warrant the assertion that the method will supplement and to some extent supersede the more indirect methods at present in use.

Department of Physical Chemistry,
University of Bristol,
England.
October 2, 1925.

STUDIES ON THE CHEMISTRY OF GOLD

BY VICTOR LENHER AND C. H. KAO

It has been shown by one of us[1] that chloride of gold can be extracted from an acidified aqueous solution by certain aliphatic esters.

It has since been found that this property differs widely among individual members and is independent of the solubility of the organic compound in water and of water in the organic compound. Ethyl acetate, which is somewhat soluble in water, gives a better extraction of gold chloride than isobutyl propionate which is practically insoluble. On the other hand, diethyl malonate which is insoluble in water gives an excellent extraction.

In view of these facts, the whole subject has been studied by determining the partition coefficient of chloride of gold in water and esters under well defined conditions.

Procedure. Hydrochlorauric acid was prepared by solution of gold in aqua regia with excess of hydrochloric acid and evaporation over calcium chloride. The resulting product as shown by Lengfeld has approximately the formula $HAuCl_4 . 3H_2O$. Standard solutions of this salt were prepared, their gold content being determined by analysis. The esters used were all prepared by us.

20 cc portions of the chloride of gold solution and 20 cc of the ester were shaken in a thermostat at 20°. The system was allowed to stand only so long as was required to allow the two liquids to separate which was determined to be in most cases, five minutes. On long standing most of the esters hydrolyse and in some of them reduction takes place with the precipitation of metallic gold. The two liquids were then separated by a separatory funnel. The gold in the aqueous layer was determined by precipitation by sulfur dioxide, that in the ester by difference.

Attempts have been made to obtain the molecular weight in various esters, but have been unsuccessful, metallic gold being produced.

A study has been made of the distribution data of $HAuCl_4$ between water and a large number of esters, and a distribution of the second order has been shown to exist in all cases. The following were used; methyl acetate, methyl propionate, methyl butyrate, ethyl formate, ethyl acetate, ethyl propionate, ethyl butyrate, isopropyl formate, isopropyl acetate, isopropyl propionate, isopropyl butyrate, isobutyl formate, isobutyl acetate, isobutyl propionate, isoamyl formate, isoamyl acetate, isoamyl propionate, isoamyl butyrate. The acetates in general are better extracting agents than any other members while the ethyl esters are in general better than any other type. As the number of carbon atoms increases the extractive power decreases. Thus it has been found that ethyl acetate gives the best extractions.

---

[1] Lenher: J. Am. Chem. Soc., **35** 546 (1913).

[2] Lengfeld: J. Am. Chem. Soc. **26**, 324 (1901).

Influence of various amounts of hydrochloric acid on the partition coefficients. The effect of hydrochloric acid in varying amounts from 1% to 30% has been determined. The presence of hydrochloric acid is a very important factor on the partition coefficient. The separation of gold chloride into the ester layer successively increases until at approximately 10% concentration the maximum extraction is reached. Further addition of hydrochloric acid beyond this point of 10% has very little influence on the partition coefficient. At 30% concentration of HCl, the esters and water are miscible. Therefore considering all of the factors involved, it appears that ethyl acetate in 10% hydrochloric acid is the most efficient extraction agent for gold chloride.

To test the general applicability of the use of ethyl acetate as a means of purification of gold chloride, and separation from the chlorides of other metals, a number of experiments have been conducted to that end. The procedure is to treat a 10% hydrochloric acid solution of the particular chloride in a separatory funnel with an equal amount of ethyl acetate and shake vigorously. The two layers are allowed to settle after which they are separated. The ester layer is washed twice with small amounts of 10% hydrochloric acid. The combined aqueous solutions are again extracted with ethyl acetate until the ethyl acetate is colorless, which requires about four extractions.

The gold is then determined by evaporation of the ester and precipitation by sulfur dioxide.

	Gold Chloride alone		*Average*
Number of Determinations	Au taken	Au found	Error
2	0 0444	0.0443	— 0001
2	0 3987	0.3986	—.0001

Separation from Sodium Chloride

Number of Determinations	NaCl taken	NaCl found	Error	Au taken	Au found	Error
6	.5849 gm	.5850	±.0004	.1148	.1149	— 0005

Separation from Potassium Chloride

	KCl taken	KCl found	Error	Au taken	Au found	Error
5	.5326	.5323	—.0004	.1148	.1147	— 0001

Separation from Magnesium Chloride

	$MgCl_2$ taken	$MgCl_2$ found	Error	Au taken	Au found	Error
4	.2992	.2995	+.0004	.1378	.1377	—.0001

Separation from Barium Chloride

	$BaCl_2$ taken	$BaCl_2$ found	Error	Au taken	Au found	Error
4	.4937	.4935	±.0004	.1378	.1375	.0003

Separation from Ferric Chloride

Number of Determinations	$FeCl_3$ taken	$FeCl_3$ found	Error	Au taken	Au found	Error
3	.4218	.4218	±.0003	.1148	.1146	±.0002
2	.2109	.2105	−.0004	.1148	.1144	−.0004

Separation from Aluminum Chloride

	$AlCl_3$ taken	$AlCl_3$ found	Error	Au taken	Au found	Error
	.4332	.4333	±.0006	.1378	.1375	−.0003

Separation from Strontium Chloride

	$SrCl_2$ taken	$SrCl_2$ found	Error	Au taken	Au found	Error
4	.3243	.3240	−.0003	.0763	.0759	−.0004

Separation from Calcium Chloride

	$CaCl_2$ taken	$CaCl_2$ found	Error	Au taken	Au found	Error
5	.5322	.5328	±.0004	.1258	.1255	−.0003

Separation from Chromium Chloride

	$CrCl_3$ taken	$CrCl_3$ found	Error	Au taken	Au found	Error
3	.1609	.1606	−.0003	.1761	.1762	+.0001

Separation from Manganous Chloride

	$MnCl_2$ taken	$MnCl_2$ found	Error	Au taken	Au found	Error
5	.5085	.5082	−.0003	.1378	.1375	−.0003

Separation from Cobalt Chloride

	$CoCl_2$ taken	$CoCl_2$ found	Error	Au taken	Au found	Error
4	.5816	.5812	−.0004	.1148	.1146	−.0002

Separation from Nickel Chloride

	$NiCl_2$ taken	$NiCl_2$ found	Error	Au taken	Au found	Error
4	.5055	.5055	±.0004	.1148	.1146	−.0002

Separation from Zinc Chloride

Number of Determinations	$ZnCl_2$ taken	$ZnCl_2$ found	Error	Au taken	Au found	Error
4	.4038	.4035	+.0005	.1148	.1147	−.0001

Separation from Mercuric Chloride

	$HgCl_2$ taken	$HgCl_2$ found	Error	Au taken	Au found	Error
4	.5020	.5021	±.0002	.1148	.1146	−.0002

Separation from Copper Chloride

	$CuCl_2$ taken	$CuCl_2$ found	Error	Au taken	Au found	Error
4	.4712	.4710	±.0002	.1148	.1147	±.0002

Separation from Cadmium Chloride

	$CdCl_2$ taken	$CdCl_2$ found	Error	Au taken	Au found	Error
4	.4945	.4942	±.0003	.1148	.1146	±.0002

Separation from Lead Chloride

	$PbCl_2$ taken	$PbCl_2$ found	Error	Au taken	Au found	Error
3	.0406	.0403	±.0003	.1375	.1373	−.0002

Separation from Bismuth Chloride

	$BiCl_3$ taken	$BiCl_3$ found	Error	Au taken	Au found	Error
4	.2763	.2759	±.0004	.1375	.1373	±.0002

Separation from Antimony Trichloride

	$SbCl_3$ taken	$SbCl_3$ found	Error	Au taken	Au found	Error
4	.2548	.2545	−.0003	.1375	.1374	−.0001

Separation from Arsenic Acid

	H_3Aso_4 taken	H_3Aso_4 found	Error	Au taken	Au found	Error
3	.3654	.3652	±.0004	.1378	.1375	±.0003

Separation from Stannic Chloride

Number of Determinations	$SnCl_4$ taken	$SnCl_4$ found	Error	Au taken	Au found	Error
4	.3894	.3894	±.0005	.1378	.1377	±.0003

Conclusions

It has been established that auric chloride can be separated completely from all of the more common chlorides in a solution containing 10% free hydrochloric acid by means of extraction with ethyl acetate.

Ethyl acetate is the most efficient of the esters for this separation.

The method is particularly useful in separating gold chloride from the alkaline earth metals, since the more commonly used sulfur dioxide will form with them insoluble sulfates.

THE PHOTOCHEMICAL OXIDATION OF LEUCO-BASES*

BY B. H. CARROLL

Although the early division of the spectrum into actinic, visible, and heat radiation has been abandoned, cases of photochemical reactions which are primarily sensitive to the longer wave lengths, are rare enough to be of particular interest. These reactions are generally oxidations.

It has been known for some time that the oxidation of leuco-bases to the corresponding dyes is accelerated by light; this photo-oxidation from the colorless base to the intensely colored dye obviously making possible a photographic process in which the leuco-base is the sensitive material, and the image is composed of dye instead of silver. Studies of the reaction by Gros[1], Konig[2], and Eder[3] demonstrated at least qualitatively, that the maximum of absorption of the dye coincides with that of sensitivity of the leuco-base. The process accordingly appeared to offer a possibility for photography of the red and short infra-red.

A study of the literature, supplemented by experiment, makes it appear probable that only the dyes of the triphenylmethane and xanthene series form stable and photosensitive leuco-bases. Other series are excluded because of instability of the bases in the dark, as in the case of the indigoid dyes, or lack of photosensitivity, as in the case of the indamines.

The malachite green series (derivatives of diparaaminotriphenylmethane) were finally selected because of their selective absorption of the red. Synthesis of the leuco-bases being found more satisfactory than reduction of the commercial dyes, four were prepared by the former method; leuco malachite green, leuco brilliant green, and two bases not in commercial use, obtained respectively by the condensation of benzylethylaniline with benzaldehyde, and of dimethylaniline with furfural. These will be designated as light green and furfural green respectively.

König established that the incorporation of the bases in collodion films not only provides a practicable form for photographic use, but also accelerates the photooxidation. The absorption spectra were found to be only slightly displaced toward the longer wave lengths, the maxima being as follows: malachite green 624 mμ, brilliant green 628 mμ, light green 628 mμ, furfural green 634 and 480 mμ. As the sensitivity of the plates so prepared is about that of "printing-out" paper, the investigation resolved itself principally into search for a sensitizer. Solutions of the leuco-base and sensitizer were mixed with the collodion, and plates were coated so as to give approximately 0.6 mg. collodion and 0.3 mg. base per cm^2. In preliminary tests they were exposed as soon as dry to a 250-watt gas-filled tungsten light at a distance of 30 cm. for 30 minutes. The plates being too insensitive for spectrograph exposures, the relative color sensitivity was tested by exposing part of the plate under Corning ruby glass, absorbing completely below 600 mμ, and another part under a Wratten H filter, absorbing above 520 mμ. The plates were fixed in changes of benzene, which was found to be quicker and less destructive to the film than the 10% aqueous solution of monochloracetic acid recommended by König. The extent of the reaction was measured in terms of density at 620-640 mμ, using a Fabry-Buisson microphotometer and a monochromatic illuminator as source of light. (Density, in the photographic sense, being the negative logarithm of transmittancy, is proportional to the dye per unit area, assuming Beer's law).

---

*Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Gros: Z. physik. Chem. 37 157 (1901).

[2] Konig: Z. angew. Chem. 17 1633 (1904).

[3] Eder: Sitzungsber. Akad. Wiss. Wien, 128 IIa. April (1919).

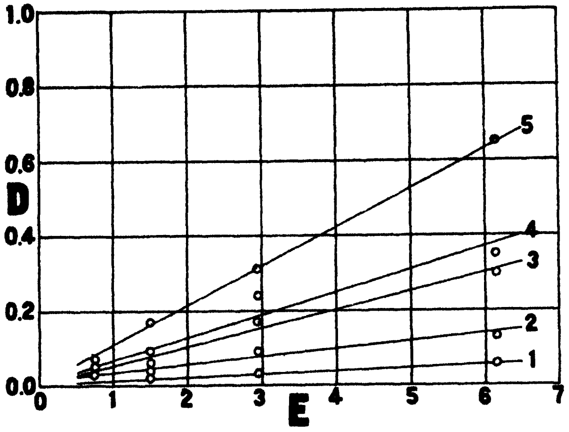


Fig. 1

Characteristic curves of leuco-base plates. Density at 620-40 mμ, plotted against exposure in candle-meter-seconds times 10^6.

1. Unsensitized light green.
2. Light green sensitized by addition of quinoline.
3. Light green sensitized by addition of mannitol hexanitrate.
4. Light green sensitized by addition of quinoline and mannitol hexanitrate.
5. Unsensitized malachite green.

Altogether some forty compounds were tried as sensitizers of one or more of the four leuco-bases. As might be expected, all four were similarly affected by a given compound. In general, the most photosensitive combinations oxidized the most rapidly in the dark, and while materials were found which accelerated the "light" reaction more than the "dark" reaction, nothing was discovered which gave promise of a stable plate of practicable speed. We therefore discontinued work on the process, although the reaction is worthy of further study for its scientific interest. The results may be briefly summarized:

1. Bases accelerate the oxidation and free acids retard it, both in light and dark. König's discovery of the sensitizing action of quinoline is a special case of this rule; the heterocylic and aliphatic amines are more efficient than the aromatic

2. The nitric acid esters were the only oxidizing agents found to accelerate the light reaction relatively more then the "dark" reaction.

3. For the four bases tested, the greater the molecular weight of the group attached to the amino nitrogen, the better the stability.

The data in Table I indicate the relative spectral sensitivity and stability of three of the bases, sensitized with quinoline and mannitol hexanitrate; the leuco furfural green was too readily oxidized in the dark for quantitative measurements. Densities being additive, the density of the unexposed portion of the plate has been subtracted from the exposure values.

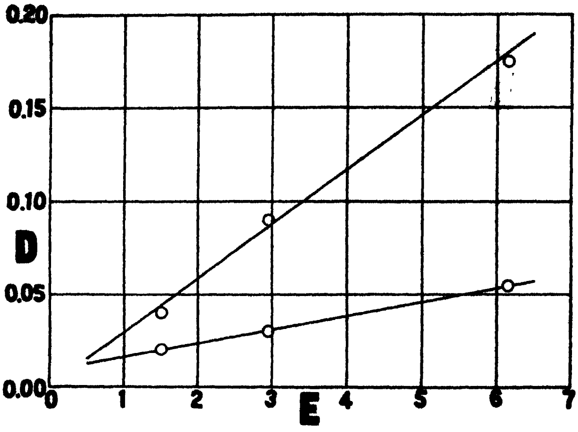


Fig. 2

Characteristic curves of leuco light green plates, unsensitized. Lower curve, exposure started forty minutes after pouring; upper curve, exposure started one hour forty minutes after pouring.

TABLE I

Dye	On Complete oxidation	After 3 Days in dark	Density at 620-40mμ		
			Direct	After Exposure Red glass	H filter
Malachite green	3	3	1.05	0.63	0.13
Brilliant "	1.9	1.9	0.17	0.05	0.06
Light "	1.45	1.01	0.62	0.59	0.13

The relation between exposure and density was tested with an optical wedge (an Eder-Hecht "Kopier-Photometer"). This gives an intensity scale of exposure; the results with a time scale would be complicated by the rapid oxidation in the dark. The curves in Figs. 1 and 2 all show that within the limits of error, the dye formed in a given time is proportional to the intensity of light. The sensitivity of these materials is measureable in terms of the slope of the density-exposure curve, rather than as the reciprocal of inertia, as in the case of the silver bromide-gelatine emulsion; all curves appear to pass through the origin, without indication of an induction period. The sensitivity of the plates increased for a time after drying. This was particularly noticeable with leuco light green, the most stable of the bases; the magnitude of the effect is evident from Fig. 2.

Discussion

The reaction is interesting not only because of unusual sensitivity to the longer wave-lengths, but also as an illustration of the different mechanisms by which added materials may influence a photochemical reaction. The amino bases do not affect the absorption of radiant energy, but increase the reactivity of the system. The nitric acid esters undoubtedly increase the reactivity of the system, yet their superiority over other oxidizing agents is probably due to their known sensitivity to light of short wave-lengths, so that at least part of the sensitivity of the plates to this region may be due to the leuco base acting as acceptor for the oxygen liberated in the photolysis of the collodion. The action of the dye formed by the oxidation of the base must, in the absence of a better understanding, be termed purely catalytic. Red light, absorbed by the dye but not by the base, is unquestionably effective in the oxidation of the latter. The experiments of Gros proved that the dye attains its maximum effect at very low concentrations; if this were not the case, the velocity of the oxidation would increase as it went on, and the observed proportionality between exposure and reaction (measured as density) would be impossible. We are therefore forced to ascribe the increase in sensitivity of the plates on standing to an unknown change in reactivity, rather than to the increase in dye resulting from the dark oxidation.

Summary

The photochemical oxidation of leuco bases offers little hope of utility as a photographic process, but it may be followed quantitatively by optical methods of analysis, and is well adapted to study of photochemical catalysis.

THE ADSORPTION OF IONS ON A MERCURY SURFACE[*]

BY W. A. PATRICK AND P. W. BACHMAN

It is the purpose of this paper to present a brief preliminary statement concerning the unequal adsorption of ions by mercury from dilute aqueous solution of mercury salts. The work has been done in this laboratory during the last year, and although not completed in all its details, it was thought best to give a brief description at this time, inasmuch as the essential points have been satisfactorily verified experimentally. Later on, a more comprehensive report, together with complete description of apparatus, etc., will be submitted.

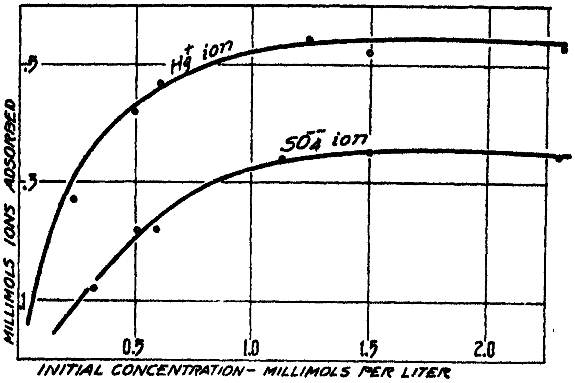


Fig. 1

Adsorption in $HgHSO_4$ solution

The experiments consisted in forcing pure mercury, by slight pressure, through chamois skin directly into a column of dilute aqueous mercurous sulphate or mercurous acetate. The glass tube which contained the solution was about four feet long and one inch in diameter. The mercury, issuing through the chamois in small drops, fell through the solution by gravity, and was collected at the bottom of the tube which was so arranged as to allow the mercury to drain off automatically. In passing through the column of mercury solution, the mercury drops adsorbed certain amounts of cations and anions. The amounts adsorbed were determined by analyzing the solutions both before and after a run. The analyses were made by electrolyzing the solutions with platinum electrodes under the proper conditions of current density, etc. The mercury depositing on the cathode was weighed directly, while the concentration of the sulfate ion or acetate ion was determined by titrating the remaining solution with standard sodium hydroxide. In this manner the amount of each ion removed by adsorption could be accurately determined. By varying the initial concentration of the electrolyte, and keeping the time, during which the mercury was allowed to fall through, constant,—the amounts of ions adsorbed at different concentrations could be compared. In regard to this, it must be remembered that although the actual mercury surface exposed during a run could not be determined with great accuracy, the working conditions were such as to make all experimental results strictly comparable. (See later paper.) It is also necessary to mention that in the case of mercurous sulfate, it was shown by electrolytic analytical methods that the ratio of mercury to sulphate corresponds to the formula $HgHSO_4$.

---

[*] Contribution from the Chemical Laboratory of Johns Hopkins University.

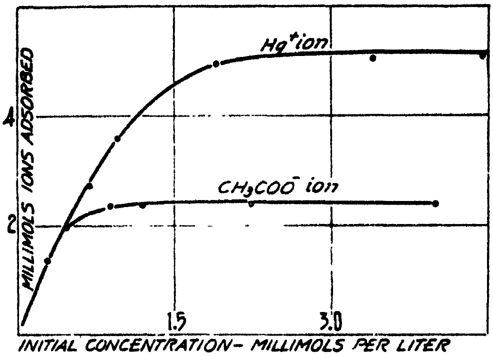


FIG. 2

Adsorption in $HgCH_3COO$ solution.

The results of the above experiments are best illustrated by the accompanying curves (Figs. 1 and 2) which show that, contrary to previous ideas concerning these systems, the mercurous ion is adsorbed to a much greater extent than either the sulfate or acetate ion. Of course, if the length of time of run is changed, different amounts of ions are adsorbed,—but the mercury ion always to the greater extent. The curves of Fig. 1 and 2 are obtained from runs all extending over the same period of time—approximately eight minutes.

In a later paper more complete results will be given, including the effect of acids and other electrolytes on the adsorption, the approximate thickness of the adsorbed layer of ions, and the corresponding effects attending the use of an adsorbent other than mercury. Furthermore an attempt is being made to correlate the experiments with absolute electrode potentials and the modern ideas concerning solutions of strong electrolytes.

Summary

It has been shown that when mercury droplets are allowed to pass through dilute aqueous solutions of mercurous sulfate or mercurous acetate, the mercurous ions are adsorbed to a definitely greater extent than the sulfate or acetate ions.

NEW BOOKS

Radioactivity. *By K. Fajans. Translated by T. S. Wheeler and W. G. King. 22 × 15 cm; pp. xii+198. New York: E. P. Dutton and Company, 1922. Price $3.50.* The chapters are entitled: the study of the chemical elements previous to the study of radioactivity; the radioactive transformations of the elements; the chemistry of the radio-elements; the displacement laws and their application; the end-products of the disintegration series and the isotopic varieties of lead; isotopy in ordinary elements; the atomic numbers of the elements; the artificial decomposition of atoms; the composition of atom-nuclei; the properties of isotopes; retrospect and prospect.

"Attention must be drawn to the fact that the half-life periods of the radio elements lie between such enormously wide limits as 10^{10} years for thorium and 10^{-11} seconds for thorium C." p. 26.

"According to one view, first put forward by Boltwood (1905), lead is the end-product of the uranium-radium-polonium series. This view is based mainly on the fact that lead is found in all uranium minerals, and in amounts which, in minerals of equal geological age, are in proportion to the uranium content, whilst in minerals of different ages, the proportion of lead varies directly with the age. This is to be expected if lead is actually formed by the slow disintegration of uranium, and so accumulates in the mineral; atomic weight considerations also seemed to support this view. Taking the earlier values for the atomic weight of uranium-I (238.5) and radium (226.4) the atomic weight of RaG was found by the usual calculation to be 206.5 or 206.4 respectively. Among the ordinary elements this agreed most closely with the atomic weight of lead (207.1); the discrepancy was thought to be due to small inaccuracies in the atomic weights. However, the revision of the atomic weights involved did not decrease the difference, but made it considerably larger. Calculated from the present values for the atomic weights of uranium-I (238.2) and radium (226.0), the atomic weight of RaG is 206.2 and 206.0 respectively, whilst that of lead, according to the latest determinations is 207.20.

"The arrangement of the radio-elements in the periodic system and the conception of isotopy indicated an explanation of this seeming anomaly, and simultaneously led to important revelations concerning the nature of the other "end-products." The application of the displacement laws to the transformations of the six radio-elements above shows that their end-products all belong to the lead-pleiad. As far as the qualitative chemical behaviour is concerned this result is, for RaG, in excellent agreement with Boltwood's hypothesis. Consequently the anomaly in the atomic weights is explained if it be assumed that RaG, that is the "lead" present in uranium minerals, has the same chemical properties as ordinary lead but not the same atomic weight; i.e. they are not identical, but isotopic," p. 47.

"From a thorianite from Ceylon, containing 68.9 percent thorium and 11.0 percent uranium Hönigschmid has isolated a lead which is obviously a mixture of thorium-lead and uranium-lead, and its combining weight (207.2) is identical with the atomic weight of ordinary lead. This thorianite-lead still shows its radioactive origin, as it possesses the activity of the lead isotope radium-D which was separated with it from the mineral. In about 200 years, however, when the radium-D (half-life period sixteen years) has practically completely disintegrated, this lead will be indistinguishable from ordinary lead, provided always that the same qualitative and quantitative chemical methods are used. Hence it is not impossible that ordinary lead is such a mixture of thorium-lead and uranium-lead. Baxter and Grover investigated seven samples of ordinary lead obtained from very different mineral and geographical sources and, allowing for experimental errors, all had the same atomic weight; this proves that even if ordinary lead is a mixture its composition is everywhere the same. This is not so strange as might appear, for both uranium and thorium must have existed before the earth's crust solidified, and consequently uranium-lead and thorium-lead must have been present in the fused mass, hence it is only necessary to assume that they then mixed homogeneously in order to explain the constancy of the atomic weight of ordinary lead," p. 52.

"The above considerations give precision to the assumption, based on radioactive data, that helium is a constituent of other elements; they show that it is the helium nucleus which is contained in heavier nuclei and not the whole helium atom. This also applies to the hydrogen atom which, as will be shown in the following chapter, also enters into the structure of other elements. Since negative electrons are contained in the nuclei of some elements we conclude that even these minute nuclei are complex structures in which enormous electrical forces must be confined. This conclusion will be of great importance in the complete explanation of Prout's hypothesis. All large deviations from this hypothesis appear possible of explanation by assuming the elements in question to be isotopic mixtures; but certain smaller deviations cannot be accounted for in this way. Thus though it is highly probable that the helium nucleus (α-particle) which possesses the mass 4.00 and a double positive charge, is composed of four simple positively-charged hydrogen nuclei each of mass 1.008, together with two negative electrons; yet its mass is not exactly 4×1.008. According to the views set out above it should be possible to reduce the mass of atoms to the masses of their constituent positive and negative particles. Now the mass shown by moving negative electrons and positive hydrogen nuclei can be ascribed on the electromagnetic theory to the electrical and magnetic forces ("electro-magnetic mass") which originate from spherical particles carrying surface charges if it is assumed that the radius of the negative electron is of the order 10^{-13} cm. and that of the hydrogen nucleus is even smaller. Since the radius of the α-particle is also only of the order of 10^{-13} cm. (evidence for this will be given in the next chapter) the electromagnetic forces, regarded as mass, which are produced as a result of the common movements of the closely-packed constituents of the particle, will influence one another. From this it can be seen that the mass of the helium nucleus need not be equal exactly to four times the mass of the hydrogen nucleus (Harkins). A similar mutual electromagnetic action between the constituents of heavier nuclei can be assumed in order to explain those finer deviations from Prout's hypothesis, which may be expected to occur in other elements. The principle of relativity supplies another explanation; this will be discussed in the next chapter," p. 76.

"Darwin has calculated that the velocity imparted to a hydrogen nucleus which has been hit centrally—the most favourable case—will be 1.6 times greater than the velocity of the impinging α-particle which has four times the mass. Theoretical considerations show that such an H-particle possesses very nearly the same range as an α-particle of equal velocity and since the range of an α-particle is proportional to the cube of its velocity, the H-particle impelled by central impact should have about four times the range of the original α-particle.

"Indeed Marsden (1914) proved that this deduction was correct. Although the range of α-particles from radium emanation contained in a very thin-walled tube was 24 cm. in hydrogen at atmospheric pressure, yet scintillations could still be observed on a zinc sulphide screen at a distance of over 80 cm. from the tube. That these scintillations were caused by simple positively-charged particles of unit mass—H-nuclei—of very high velocity was proved by measuring the deflexion of these particles in electrical and magnetic fields," p. 80.

"There are those who still hold that chemically isotopes are to be regarded, not as very similar, but as absolutely identical. The theoretical and experimental results discussed in this chapter leave little doubt that this view is incorrect, for spectroscopic measurements of isotopes have shown differences both in the oscillations of the electrons situated in the outermost regions of the atoms and in those of the atoms within the molecules, and hence there must exist corresponding chemical differences; this has already been stated in Section 1. The vaporization experiments of Brönsted and v. Hevesy have proved that isotopes possess different molecular velocities; hence in a chemical reaction under favourable conditions between, for example, a gaseous mixture of isotopes and a solid substance, the rapid molecules will collide more frequently with the solid substance, so that isotopes should have different reaction-velocities and the separation of an isotopic mixture should be possible, even by 'chemical methods'.

"Strictly speaking, none of the properties of isotopes which can be determined experimentally are identical. This is true even for the electrostatic field of the nuclear charge—that fundamental property in the classification of the elements—which up till now had been assumed to be equal in isotopes. For the nuclear charge can be obtained either indirectly by the determination of other properties; for this purpose the characteristic X-rays are particularly suitable, and here the differences mentioned in Section 1 will probably be observed, or, the direct electrostatic action of the nuclei on α-particles coming into their immediate neighbourhood can be determined, as Rutherford and his co-workers have done. Assuming sufficient accuracy of measurement, the influence of the different compositions of the nuclei of isotopes should then be distinctly observed.

"Theoretically the isotopes are identical only in the equality of the algebraic sums of the positive and negative constituents of their nuclei; in all properties accessible to observation differences are to be expected. According to the view that isotopes are not different elements but merely varieties of the same element a chemical element cannot be definitely characterized by any property and certain variations in their properties have to be admitted. The fact, however, that these variations are exceptionally small for some properties but easily measurable for others, makes it possible and desirable for practicable purposes to differentiate between the two following groups of properties of isotopes. On the one hand we have, in addition to the nuclear charge, the qualitative behaviour, the general structure of the spectrum, the atomic volume, the molecular solubility of the salts, the boiling-point and melting-point and several other properties which, although not mentioned here, have already been investigated, e.g. the electro-chemical potential, the refractive index of solutions of the salts, the rate of diffusion in solution, the magnetic susceptibility, the specific electrical resistance in the metallic state and probably many other properties. Within a high degree of approximation all these properties are equal for all varieties of an element, i.e. for all members of a pleiad and their mixtures. Practically speaking they can be regarded as characteristic of the element, and can be called 'pleiad properties' or colligative properties of the isotopes. On the other hand we have the atomic weight and with it the general behaviour in quantitative analysis, the radioactive properties, the density in all states of aggregation, the solubility expressed in grams/litre, etc., which for every member of a pleiad and for every mixture of isotopes, for example, every variety of lead, have different values. These are the individual properties, and permit of a finer differentiation of matter than do the pleiad properties. It is obvious from the above that there exists no sharp limit between these two groups of properties," p. 104.

"The most important result of the investigations surveyed is the proof that the chemical elements, hitherto regarded as homogeneous are composite. Many of them are mixtures of isotopes, so that the atomic weight (combining weight) of these elements, hitherto so fundamental, is only a mean value of other numbers possessing a much deeper scientific significance. In their turn the single atoms have come to be regarded as being built up from the two simplest atoms, hydrogen and helium, in a way quite different. The latter is most probably formed from four atoms of hydrogen in particularly close combination; and Proût, over 100 years ago, similarly assumed that hydrogen could be regarded as the constituent of all other atoms. But even the hydrogen atom is composite, consisting as it does of one atom of positive, and one of negative, electricity; electricity then is the long-sought primordial matter, of which all elements and consequently the whole material world are constructed," p. 114.

Wilder D. Bancroft

Die Methoden der Organischen Chemie. *By J. Houben (and collaborators). 17 × 26 cm; pp. xxviii+1340. Leipzig: Georg Thieme, 1925. Price: paper 66 marks, cloth 75 marks.* With the exception of those whose long experience serves them better than any practical text-book, there can be few organic chemists who do not turn up "Houben-Weyl" as a matter of course as each fresh problem is encountered. The publication of a new and enlarged treatise on the practical methods of organic chemistry is therefore an event of interest.

The first volume, here under review, deals with the analysis and physical examination of organic compounds and with the physical processes used in their preparation and purification. It makes, perhaps, a special appeal to those whose problems often demand resort to physical methods. Within its 1300 pages, copiously illustrated, are contained detailed accounts of the standard methods for estimating elements and radicals in organic compounds, of the common operations of preparative work (including the handling of gases and colloids), and of the methods for determining such data as melting point, boiling point, solubility, density, molecular weight, optical rotation, refractive index, conductivity, hydrogen-ion concentration, intensity of fluorescence, heat of combustion, ignition-temperature, viscosity, etc.

In view of the recent introduction of Pregl and Dubsky's micro-analytical methods into many University and other laboratories the chapter on micro-analysis, written by Dubsky, will be widely read, and will doubtless do much to disseminate knowledge of these rapid and elegant processes, some skill in which will in future constitute a necessary part of the manipulative equipment of all research workers.

It is perhaps the inevitable consequence of an attempt at completeness that parts of the volume are of interest mainly to specialists, who, as a matter of fact, would probably turn for their information to special sources rather than to a general text-book of practical organic chemistry. Such, for example, are the sections on ultra-filtration, adsorption-analysis, interferometry, goniometry and the analysis of dyes. Yet, in spite of the wide scope of the work there are some surprising omissions. Thus it is curious that, in the chapter entitled "Erhitzen", one may read a detailed description of all the methods that have been devised for maintaining a constant level in a water-bath, but may look in vain for some simple directions for fixing up an electrically controlled thermostat. Considerable space is devoted to description of the old methods of plotting "absorption spectra", and, regardless of the fact, for years past generally recognised, that such determinations are meaningless from the quantitative standpoint, no account is given of the spectra-photometric apparatus whereby the variation with wave-length of the intensity of the light-source and sensitivity of the plate, and the variable absorption of the solvent if one is used, can be automatically eliminated and a quantitative absorption curve obtained. The section on magnetic rotation might well have been extended in view of the ease with which the ordinary polarimeter can be adapted for the determination of magnetic rotations. But these and other lacunae will probably not often be encountered when referring to the book in the course of ordinary laboratory practice, and it remains true that the new "Methoden" contains a wealth of useful information the collection of which under one cover is of great importance for all organic chemists. The succeeding volumes of this work will be awaited with interest.

C. K. Ingold.

A Course of Metallurgy for Engineers. *By F. C. Thompson. 15 × 22 cm; London: H. F. and G. Witherby, 1925. Price: 25 shillings.* Professor Thompson's book is the outcome of many discussions with Mr. W. E. W. Millington. It represents the cooperation of a metallurgist and an engineer and is designed as the title indicates, to instruct the engineer as to the nature of the metals used by his profession. As the author points out in his preface, although the Institution of Mechanical Engineers has by means of its Alloys Research Reports added materially to metallurgical knowledge over a long period, engineers were until recently, for the most part, deplorably ignorant of the structure and nature of the metals and alloys which they use.

The first chapter contains a brief account of the principal commercial ferrous alloys and their manufacture. Then follows one on the composition and structure of steel. The four succeeding chapters deal with ingots and ingot defects, the heat treatment of steels and the hot and cold working of steel. A special chapter is devoted to tool and case-hardening steels and another to cast iron. The latter section of the book is concerned with the principa non-ferrous industrial alloys, *e.g.* brass, bronze, alumnium alloys, and bearing metals.

Other books have been written purporting to instruct the engineer in metallurgicl knowledge. None of them, however, have been quite of the right kind. For the mot part, they have not credited him with much intelligence. On the one hand, they have given him, at unnecessary length, elementary metallurgical knowledge of a kind that he does not particularly need, and, on the other hand, they have generally failed to tell him things which would be of the utmost importance to him. Although Professor Thompson is very modest about his book and writes that he "is woefully aware of its defects", we think that he has written by far the most useful book for engineers that has yet been published. He has assumed that the engineer possesses average intelligence in following a scientific argument. He has not overburdened his book with technical terms and for this the engineer will be grateful. The treatment throughout is scientific but the illustrations are always drawn from alloys well known and widely used. The engineer who is really interested in the structure and properties of the metals that he uses, will find this book of very real interest and value. He will probably need to supplement the knowledge obtainable in it with that contained in a good text-book of metallography written rather more from a metallurgical standpoint. Particularly will this be the case in reference to the interpretation of equilibrium diagrams which are only treated incidentally in the book under review. The equilibrium diagram is the sheet anchor of the metallurgy of alloys and we think the author might with advantage have given a rather fuller and more direct treatment of this branch of the subject. It is possible that Mr. Millington will not agree with this criticism, but it is perhaps worthy of being taken into consideration.

It is very unfortunate that the price of this book is so high. It ought to be very widely studied by engineers but unless its price is considerably reduced we fear that this is not likely to be the case. Could not the publishers, in a subsequent edition, reduce the price from 25/ to 15/? It will make all the difference to the sale of the book.

H. C. H. Carpenter.

The Textile Fibers. *By J. Merritt Matthews. Fourth edition, rewritten and enlarged. 23 × 16 cm; pp. xviii+1053. New York: John Wiley and Sons, 1924. Price· $10.00.* The third edition was reviewed nearly twelve years ago (**18**, 454). The present one is fifty percent larger than its predecessor, besides differing in other ways. The chapters are entitled: general classification; asbestos as a textile fiber; wool, its origin and classification; physical structure and properties of wool; the chemical nature and properties of wool and hair fibers; action of chemical agents on wool; reclaimed wool and shoddy; minor hair fibers; silk, its origin and cultivation; physical properties of silk; chemical nature and properties of silk; the vegetable fibers; cotton; the physical structure and properties of cotton; constituents of raw cotton; cellulose and its chemical properties; chemical properties of cotton; chemical treatment of fabrics for waterproofing and flame proofing; mercerised cotton; the minor seed hairs; artificial silks; linen; jute, ramie and hemp; analysis of fibers and yarns in fabrics.

Spun glass is made in a very simple way. "Solid glass rods, about 2 ft. 6 ins. long and of the thickness of a lead pencil, are made of pure soda glass that contains no adulteration of lead or other metal. The absence of lead and adulterations gives the quality of perfect flexibility to the fiber. On a simple desk is mounted a Bunsen burner or gas flame and blowpipe. By the side of the desk is mounted an ordinary bicycle wheel, minus the rubber tire, that revolves rapidly and regularly at rhythmic speed under power furnished by a small electric motor. A girl sits at the desk, melts the end of the glass rod in the flame of the gas burner, draws it to a thread and throws the thread around the wheel. If the thread breaks, she must repeat the process; if not, she slowly revolves the end of the rod in the constant flame, and it is automatically spun to a very thin filament. The hank of thread on the wheel, when it has assumed the dimensions of a bicycle tire, is taken off. Separated with the fingers, it curls and fluffs out like wool if the thread is sufficiently fine. It is packed in the hank as glass cotton, in the fluff as glass wool, and in the compressed form as glass wool or cotton according to the fineness of the fiber. The cheaper grades of spun glass formerly came from Germany; it is claimed that the Italian article is superior," p. 11.

"There can be little doubt that there is a definite relation between the softness of the asbestos fiber and the quantity of water of constitution it contains; 14.38 percent water has been found in very silky fiber, while a harsh, brittle sample gave only 11.7 percent.

This will explain the extreme brittleness of the amphibole fiber, some samples of which contain only 5.45 percent water. The effect of high temperatures on very soft fiber also demonstrates this fact. When part of the combined water has been driven off by excessive heat, the fiber loses its flexibility and becomes harsh and brittle; and the variations in strength and silkiness in various deposits of the mineral are best explained by assuming that the water content was originally nearly the same in all cases, and that the movement of associated rocks or the injection of molten rock has furnished sufficient heat to drive off part of the water," p. 31.

"The felting action of wool, however, must not be attributed solely to the interlocking of the scales on the surface of the fiber. This has been the general conception in the past, but the examination of felted fibers does not bear out this idea. If the felting were altogether due to the interlocking of the scales it would require that two fibers be brought together in opposite directions in order to have this interlocking take place. As a matter of fact, in a piece of felted cloth for example, the wool fibers are located in all manner of directions and only a small percentage of them would be juxtaposed in such a manner as to furnish the necessary conditions for felting by interlocking of the scales. The felting is largely due, in the first place, to the intermeshing of the fibers themselves by becoming twined round one another, and this condition is especially enhanced by the curl in the fiber. Again, in the felting operation of milling or fulling, the surface of the fiber no doubt is softened in such a manner that fibers coming in contact with one another and, under the influence of heat, pressure and the chemicals employed, become more or less glued together. As the substance of the scales of the fiber is in reality a form of glue or gelatine, it is easy to understand why this condition can readily be induced by the felting process. Microscopic examination of the intimate structure of felted fibers indicate a strong surface cohesion rather than a mere interlocking of the scales. This also explains why it is perfectly possible to felt wool fibers that do not exhibit well-defined free scales Hair, though it has the surface scales, does not have these scales arranged so as to show very much free edge projecting from the surface of the fiber; also these scales are hard and not easily softened to the point where strong cohesion may take place between fibers in contact with one another. If, however, the surface scales are softened so that they become somewhat mucilaginous in character, then by heat and pressure hair fibers may also be felted much in the same manner as ordinary wool fibers," p. 91.

"When wool is treated with a four percent solution of formaldehyde it is made much more resistant to alkalies and also shows a decreased affinity toward dyestuffs. Kann has described this use of formaldehyde as a means of dyeing wool with vat dyes in which a strongly alkaline bath is employed. The formaldehyde may be added directly to the alkaline bath. It is also claimed that sulfur dyes may be applied to wool in the same manner. Wool treated with formaldehyde is said to be much more resistant to the action of steaming than untreated wool. There have been many attempts to devise a method of treatment whereby the wool fibers could be protected from the destructive action of the alkali which is required in dye baths employed for these colors. Kann has taken out a number of patents during the last few years describing the use of formaldehyde for this purpose. It was first recommended to employ a four percent solution of formaldehyde for the treatment of the wool, but it is now pointed out that the use of such a solution, although protecting the wool to a considerable degree against action of the alkali, decreases greatly its affinity for dyestuffs. In later patents formaldehyde was added to the alkaline dye bath, and it was eventually discovered that only small quantities of formaldehyde are necessary to produce the desired effect. When used in these proportions the formaldehyde does not decrease the affinity of the wool fiber for dyestuffs," p. 166.

"As regards the influence of tin weightings, whether simple or mixed, upon dyeing, they are all perfectly suitable for any color, and both for cuit and souple silks. The black-dyer is less dependent than others on the weighting, as he uses substances like tannin and iron salts, which themselves act as loaders. These bodies are barred to the color dyer for the most part as they darken the fiber, and he is confined to bleached tannin, alumina, and colorless salts. Tannin is dear, always darkens the fiber, and does not give enough weight alone, although it gives far more than alumina or salts. In short, modern silk-dyeing is impossible without tin weighting. Tin can be applied at any stage of the preparation of the silk, or raw silk, to souple, or to boiled-off silk. Tinned raw silk can be scoured, without losing more tin than corresponds to the percentage of bast removed. It can be mordanted with iron, alumina, or chrome, and can be further weighted with Prussian Blue, and finally it can be dyed with natural coloring matters, or the coal-tar dyes.

"Silk-weighting is the basis of modern silk-dyeing. Any serious struggle against it is a hopeless fight against the natural development and progress, is based on mistaken ideas, and can only be useful against an exaggerated and irrational loading of the fiber," p. 312.

This argument is rather sophistical. The amount of tin that is added does not stand in any relation to the amount needed for dyeing. The weighting of silk must be judged on its merits and not with reference to dyeing.

Byssus "is also known as 'sea-silk' or 'pinna silk,' and is obtained from a marine mollusk, *Penna nobilis*, and related varieties. The shellfish possesses a long slender gland which secretes woolly fibers known as the *Byssus* or 'beard'. These fibers are of a brown color and are 4 to 6 cm. in length. The brown color is said to be due to an external covering which when removed leaves a colorless fiber. Sea-silk is somewhat used in southern Italy and in Normandy for the making of various ornamental braided articles. Though this fiber somewhat resembles silk in appearance, it is easily distinguished by the presence of natural rounded ends. The fibers vary considerably in diameter (10 to 100 microns) and are elliptical in cross-section, and are often twisted. Fine longitudinal striations are apparent, but as the fiber is solid no empty lumen or air canals are present. The finer fibers are smooth, but the coarser ones are rough and corroded. Frequently very delicate fibrils are to be observed branching from the larger fibers.

"The manufacture of materials from pinna silk was carried on at Taranto in Italy. The 'fish wool' (as it was called) was washed twice in water, once in soap and water, and again in tepid water, and finally spread out on a table to dry. While yet moist it was rubbed and separated with the hands and again spread on the table to dry. When quite dry it was drawn through a wide bone comb and then through a narrow one. It was then spun into a yarn with distaff and spindle. As it was not possible to procure much of the material of good quality the manufacture was limited to a few articles such as gloves and stockings, and these were quite expensive. The fabrics were very soft and warm and of a brown or glossy gold color," p. 316.

"It may be seen from these results of microscopic investigation that the behavior of the fibers on swelling in water is very remarkable and distinctive, and that in this particular very essential differences exist between vegetable and animal fibers.

"The investigation helps to explain the fact why ropes shorten when left in water. Fibers which are not stretched or are only slightly so, are arranged in ropes in permanently fixed spirals. Since the fibers can only be lengthened but slightly, or not at all, while they are thickened 20-25 percent by swelling, the rope as well as the single twisted fibers must become shortened. If the spiral fibers are very elastic, as is the case of the animal fibers which may be stretched 5 to 36 percent in the moist condition without breaking, then the cylinder composed of them will shorten but slightly on swelling (or even none at all), because the spirals are capable of being lengthened. Thus it has been observed that a hemp rope will shorten 8 to 10 percent, whereas a silk rope will shorten only 9.24 to 0.95 percent. Furthermore, a twisted single vegetable fiber will shorten only slightly, whereas it is easy to understand that a twisted animal fiber will perhaps become lengthened, while a silk cord is shortened," p. 346.

"Cellulose acetate is, for instance, unique in its dyeing properties, in that with ordinary methods it can be dyed only by means of basic dyes, which are among the most fugitive of coloring matters; direct cotton colors it refuses to take up, and the dyeing of fabric composed of cotton and artificial silk with direct colors, a very usual procedure, is not possible in the case of acetate silk. If this is attempted with acetate silk, the cotton takes up the color normally, but the acetate combines only with the basic impurities in the dye, with the result that the former may be the desired navy blue while the latter is perhaps a dirty yellow shade, or while the former is black, the latter is brick-red. When dyeing is attempted with vat colors of the indanthrene type, which are coming into great demand on account of their remarkable fastness and consequent suitability for washable materials, cellulose acetate silk sometimes is partly decomposed, and loses its luster and silk-like properties. Considerable effort has been made to devise methods for the satisfactory dyeing of acetate silk with substantive dyes, and it has been found that a treatment of the fiber with a solution of caustic soda (saponification) previous to dyeing gives very good results without materially affecting the quality of the silk. It is understood that the manufacturers of this silk now place the treated material on the market ready for dyeing," p. 707.

"The differences experienced in the dyeing of different forms of artificial silk are of interest. The nitro or collodion silks have a strong affinity for basic dyes and unless care is used the colors will be uneven. The cuprate silks have less affinity for basic dyes, and for the production of full shades it is necessary to mordant with tannic acid. The direct cotton dyes give the best results; sulfur dyes and vat dyes may also be used but will generally injure somewhat the luster. Viscose silk is similar to mercerised cotton in its affinity for dye-stuffs. The acetate silk as at first produced could not be dyed satisfactorily as the cellulose acetate was impervious to water, but the acetate silk now produced is partially saponified and contains hydroxyl groups which give the silk a much greater affinity for dyestuffs. Cellulose acetate silk has but little affinity for the direct cotton dyes, and in order to dye with these colors special treatment must be resorted to, which consists of working the silk in a bath of caustic soda, or in some cases the caustic soda may be employed directly in the bath with the dyestuff. This treatment does not seem to have any effect on the material nor to effect the luster. The basic dyes have a direct affinity for acetate silk and no mordanting is necessary. Many of the acid dyes are also useful for acetate silk. The new series of dyestuffs discovered by Green and known as "Ionamines" have a remarkable affinity for acetate silk and may be dyed directly on that fiber," p. 710.

"Marine fiber is a recent product obtained by dredging in the shallow water of a gulf in South Australia. Chemically it is a hydrated lignocellulose, giving the typical reactions of lignin. Microscopically it is very similar to New Zealand flax. From this it is to be concluded that the fiber is not of marine origin, but has been produced by the natural retting of a land plant, which has become submerged by the sea. Owing to its lignified character it dyes directly with basic dyes and some acid dyes, but has little affinity for substantive dyes. The fiber is brittle and has but little strength.

"Marine fiber has its origin in the leaves and stem of *Posidonia australis*. It is a submerged marine flowering plant and the enormous beds of the fiber which have been discovered appear to be due to the covering of the dead bases of the leaves and stems by the shifting sand which serves to preserve the fiber from decay. In the mass it is pale brown and somewhat lighter in color than cocanut fiber. In is estimated that the workable areas of South Australia alone would furnish 4,500,000 tons of the material," p. 807.

"Solidonia fiber is a name given to a vegetable fiber brought out in Germany as a wool-substitute. It is supposed to be a fiber derived from an African plant similar to China grass, and it seems to be very similar to ramie. It is a very fine fiber and has a screw-shaped form which makes it somewhat resemble wool. The length of the fibers varies from 2.5 to 4 ins. in length in medium grades, while the finer grades reach a length of 6 ins. According to Valdenaire, the solidonia fiber when examined under the microscope shows filaments having branches and striations, and also has a large central canal or lumen of a yellow color. The Vetillard reagent colors the fibers a greenish red, inclined to a violet. The fibers obtained from the nettle, which are somewhat similar to solidonia, are stained blue by the same reagent. In the raw state solidonia is of a gray color, similar to flax, but is bleached very easily. It acts the same as cotton in the presence of dyestuffs and the dyeing operation is the same. The property possessed by solidonia of absorbing perspiration without creating a sensation of cold on the skin, enables it to be mixed with wool to advantage in the manufacture of knit goods.

"Solidonia is converted into yarn by either the carded woolen or worsted process and is spun by the worsted process not finer than 36's (cotton count). Up to the present time the material has been used for knit goods, passementerie, in mixtures with short wool for dress goods and cheviots and in mixtures with long wool for imitation worsted.

"In Germany, solidonia gained a wide field of use on account of the shortage of wool during the War. As a substitute for linen, solidonia has been used in Germany for the manufacture of table linen of beauty and strength. It has been used for machine belting. German hosiery and underwear mills have produced from it socks and stockings which are difficult to tear, and unshrinkable underwear, and sporting jackets of fine quality and strength.

"The German woolen mills have manufactured an army cloth composed of 75 percent wool and 25 percent solidonia, which, it is asserted, surpasses in tensile strength any pure wool cloth. Similar results are claimed with respect to papermakers' felts, which, with a percentage of solidonia mixture, show a considerable increase in strength. Furthermore women's and men's clothing composed of half solidonia and half wool or shoddy, especially in piece-dyed goods, have found a ready market. In textile circles in Germany it is declared that there is an unlimited field for the use of this fiber. Previous to the War the price of solidonia in Germany was two-thirds the cost of good staple wool," p. 836.

While the author seems to have kept up pretty well so far as the technical developments are concerned, his knowledge of general theory has not gone much beyond the undergraduate stage. He speaks of alpha, beta, and gamma oxycelluloses, p. 538, as though they might exist. He believes in an alkali cellulose as a definite compound, pp. 505, 581, and ascribes mercerization to the intermediate formation of this substance. His views on dyeing, pp. 145, 550, are Botticellian in their primitiveness. One must differentiate sharply between the subjects on which the author is an authority and which constitute the greater part of the book, and the occasional ones on which he merely holds forth.

Wilder D. Bancroft

An Introduction to Organic Chemistry. *By Alexander Lowy and Benjamin Harrow 24 × 16 cm; pp. ix+389. New York: John Wiley and Sons, 1924. Price: $3.00.* The authors have tried to include "not only the well-recognized basic principles of organic chemistry, but also its more recent and more important applications; the entire story being woven together into a simple and readable narrative. The authors have also kept in mind the many connecting links that bind organic chemistry to a number of other sciences,—to medicine, dentistry, pharmacy; to agriculture; to the biological sciences; hence, the inclusion of such chapters as those dealing with lipoids; nucleoproteins and their decomposition products; the chemical changes which foodstuffs undergo in the body; plant and animal pigments; enzymes, vitamins and hormones; organic compounds of arsenic and other metals; dyes and strains, etc."

As a typical instance of what they are trying to do, let us take a paragraph, on p. 178. "In diabetes, the poisonous 'acetone bodies' or 'acid bodies,' which are so often produced, are derived from fats. These 'acetone' bodies include butyric acid, β-hydroxybutyric acid, acetoacetic acid, and acetone. The acetone is a by-product obtained probably from acetoacetic acid by the loss of CO_2. It would seem as if the diabetic has not only difficulty in oxidizing glucose, but also in completely oxidizing fats; the fats in his case are oxidized to the four-carbon stage and no farther. Working with the knowledge that the naturally-occurring fats all contain an even number of carbon atoms, and stimulated by Knoop's theory that fatty acids are oxidized in such a way as to lose two carbon atoms at each stage, Kahn has synthesized an odd-carbon fat—from margaric acid, $C_{16}H_{33}CO_2H$, a C_{17} acid—which is said to produce 'acetone bodies' when given to the diabetic, because in the oxidation of this odd-carbon fat, the four-carbon acids are avoided; thus

$$C_{17} \longrightarrow C_{15} \longrightarrow C_{13} \longrightarrow C_{11} \longrightarrow C_9 \longrightarrow C_7 \longrightarrow C_5 \longrightarrow C_3 \longrightarrow C_1"$$

On p. 307 there is a table giving the chief known constituents of thirty-nine essential oils. What the authors planned to do was worth doing. If the performance is not up to the level of the dream, that does not make the dream any less beautiful. Portraits are given of Grignard, Pasteur, Emil Fischer, Kekulé, Gomberg, Baekeland, Remsen, Perkin, and Baeyer.

Wilder D. Bancroft

FOURTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS[1]

BY HUGH S. TAYLOR

It is the object of the present report to review the problems of contact catalysis as set forth in the First Report of the Committee, in order to estimate how far, as a result of research during the last four years, these problems have approached to a definite solution; an attempt will be made to set forth a point of view whereby the various phases of the problem of contact catalysis may find a unified theoretical treatment and to outline, as far as possible, the problems for future work which this suggests. No complete survey of the year's catalytic literature has been made, because it is felt that such a survey can profitably be made at less frequent intervals.

The Mechanism of Catalytic Action

In the First Report of this Committee two distinct types of contact catalysis were apparently indicated; in the one case, catalysis was accompanied by the formation of a definite intermediate compound, while in the other case, catalysis was preceded by adsorption with activation. Examples were cited in support of both types. It was definitely pointed out, however, by Mr. Bray, that on the borderline between the two, cases might exist in which there might be indefinite intermediate compounds which could not be ascribed to either one or the other. Precision was given to this intermediate type by the example of cupric chloride as a catalyst for the Deacon chlorine process. Mr. Bray pointed out that it was not necessary to assume that a definite oxychloride of copper is produced in the conversion of hydrogen chloride and oxygen to chlorine and water. It was only necessary to assume that an exchange of oxide and chloride ions occurred at various points in the solid cupric chloride lattice[2]. The extent to which such an exchange will occur will obviously depend on experimental conditions such as oxygen and chlorine concentrations, temperature and the like. It would only be a fortuitous circumstance if these were such that on the average, half the chloride ions were replaced by oxide ions; nor, in rapid reactions, could the change be expected to extend much beyond the surface. From the subsequent discussion, it will emerge that the probable state of the surface at any moment during the change will be such that some of the lattice positions normally occupied by chloride ions in solid cupric chloride are momentarily occupied by oxide ions, the actual positions occupied by oxygen undergoing continuous change. The catalytic activity of copper chloride would then be attributable to the ease with which such exchange of ions proceeds. It is of interest to record this newer aspect of the matter since the choice of copper chloride as a catalyst was originally made from theoretical considerations, it being observed that in the case of the copper salt the energy involved in the change from oxide to chloride was a minimum. It is necessary to insist, as pointed out by Professor Bancroft that no stoichiometric relations hold for such cases—in contrast with other well-defined cases of intermediate compounds where stoichiometric relations hold rigidly. The non-stoichiometric cases are therefore best treated in the manner usual in the treatment of adsorption at surfaces.

---

[1] Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by Hugh S. Taylor, assisted by the other Members of the Committee: Messrs. H. A. Adkins, E. F. Armstrong, W. C. Bray, D. W. Brown, R. F. Chambers, C. G. Fink, J. C. Frazer, E. E Reid, and W. D. Bancroft, Chairman.

[2] The difficulty raised in the First Report as to anhydrous cupric sulphate as a catalyst for this reaction does not, in reality, exist. Dr. R. A. Beebe has shown that passage of hydrogen chloride gas alone or admixed with air over solid cupric sulphate at the temperature of the Deacon chlorine reaction results in the quantitative conversion of the sulphate to chloride. The experimental results bearing upon this will be published elsewhere. H.S.T.

Adsorption and Activation.—It was abundantly evident in the First Report that capillary condensation was not the origin of catalytic change. Catalysis could not be ascribed to the increased concentration consequent on adsorption processes, nor could alternative modes of reaction at different surfaces be explained by such concentration increases. Experimental measurements on adsorption by a variety of catalytic agents, metals, oxides and salts, the variation of the extent of adsorption with temperature, pressure, form of the catalyst and support material, as well as on the thermal magnitudes involved in such adsorption processes[1], have revealed that the adsorptions involved in catalytic change are not capillary condensation phenomena but are, on the contrary, specific in character, determined by the catalyst and by the gas, involving energy changes considerably greater than those demanded by liquefaction phenomena and approaching in magnitude those common to mild chemical reactions. The results obtained conform, in the main, though with important divergences in detail, to the concept, developed by Langmuir, that the adsorbed gas is held chemically by the unsaturated atoms at the surface of the solid. In broadest outline, Langmuir's point of view may be stated in his own words: "The surface of the metal is thus looked upon as a sort of checkerboard containing a definite number, N_0, of spaces per square centimeter. The number of elementary spaces, N_0, is probably usually equal to the number of metal atoms on the surface. But this is not essential, for, we can imagine cases in which each atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface."

Langmuir detailed in his paper on the adsorption of gases by plane surfaces of mica, platinum and glass[2], the theoretical treatment of such adsorption processes, and demonstrated that his experimental results confirmed the theory in its simpler aspects. In its more complex aspects (e.g. Cases II and IV of his theoretical treatment), in which the surface may contain several kinds of elementary spaces and may adsorb several different numbers of adsorbed atoms or molecules, the theoretical equations are so complex that no satisfactory check on their accuracy can be expected from the form of the adsorption isotherms or isochores. The writer, has pointed out, however, that in the data accumulated on adsorptions of different gases by catalytic agents, their variation with temperature and pressure, the effect of catalyst poisons on adsorption and reaction velocity, a very definite proof of the composite nature of the catalytic reaction surface can be achieved. The arguments may be briefly summarized.

---

[1] A résumé of such experimental data has already been given in the Third Report: J. Phys. Chem. **28**, 921-933 (1924).

[2] J. Am. Chem. Soc., **40**, 1361 (1918).

Varying Saturation Capacity of a Surface for Adsorbed Gases at Varying Temperatures.—The data of Gauger and Taylor[2] on adsorption of hydrogen by nickel at varying temperatures showed that, at each temperature, an upper limit to adsorption capacity was reached beyond which further increase of pressure brought about no further increase in adsorption. The upper limit of adsorption was, however, different at different temperatures. Thus, with a given sample of nickel, at 25°C., saturation was reached at 75 mm. pressure and a further ten-fold increase of pressure did not alter the adsorption (8.7 ccs.) by more than 1 per cent, the limit of experimental accuracy. At 305°C. saturation was reached at 250 mm., but, at this temperature, the adsorption was only 5.4 ccs.

Terwen[3] has sought an explanation of this varying maximum of adsorption at different temperatures, by assuming two modes of adsorption of hydrogen by the nickel atoms in the surface. At low temperatures the gas is assumed to be adsorbed as the molecule $\left(-\mathrm{Ni}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H},\end{smallmatrix}\right)$ at high temperatures as atoms $(-\mathrm{Ni}-\mathrm{H})$. Terwen points out that the data of Gauger and Taylor indicate that the maximum adsorption at high temperatures does not fall below one half of the observed adsorption at low temperatures and seems to be approaching this half-value as a limit. It should be pointed out that other gases, for example, carbon monoxide on copper, show the same varying saturation adsorption with temperature. Since there can be no question of atomic linkages in this case it would be necessary to assume that at low temperatures one atom of copper adsorbs a molecule of carbon monoxide and that at high temperatures two atoms of copper are required. In this way the experimental facts could be visualised, but proof would be difficult. Terwen suggests that proof of his point of view might be obtained from determinations of the temperature coefficient of the heat of adsorption of hydrogen, since this should change markedly with change in the type of linkage. Experimental data on this point are now being sought in Princeton. Terwen also suggests that Gauger's data[4] on the critical potentials of hydrogen adsorbed on nickel indicate the existence of atoms and molecules on the catalyst surface. Gauger's measurements are being repeated in Princeton since his experimental method is not

---

[1] Proc. Roy. Soc., **108A**, 105 (1925).

[2] J. Am. Chem. Soc., **45**, 920 (1923).

[3] Chem. Weekblad, **21**, 386 (1924).

[4] J. Am. Chem. Soc., **46**, 2880 (1924).

entirely free from objection. At the same time the effect of temperature on the results will be studied.

While Terwen's conclusions are in agreement with the adsorption data, they are difficult to reconcile with the data on poisoning and reactivity. On his view of an equilibrium between adsorbed atoms and molecules, the effect of a poison would be to cut down the total surface, but without altering the ratio of adsorbed atoms and molecules. The effect ought, therefore, to be proportional to the poison present. We shall show that abundant experimental evidence now exists that this is not always the case, that poisons reveal a varied activity of surface atoms. Consequently, the varying saturation adsorption of the catalyst surface at varying temperatures constitutes, in our view, contributing evidence in support of the view that the various atoms in the surface have varying adsorptive capacity and consequently varying catalytic activity. This does not, however, exclude the possibility that there are varying modes of attachment of the adsorbate to the adsorbent, as postulated by Terwen.

Varying Saturation Capacity of a Catalyst for Different Substances.—Two examples will be cited, neither from the Princeton work, which contains many such examples. Hirst and Rideal[1] have found that copper shows saturation capacity for both hydrogen and carbon monoxide but, in their measurements, approximately 8.5 times as much carbon monoxide is adsorbed at saturation. Maxted has recently shown[2] that both lead and mercury ions are adsorbed by platinum sols and show maximum adsorptions not varying with increase of concentration. The lead ions are adsorbed, however, 3.5 times as much as the mercury ions, although there can be no great difference in the ion sizes. These cases are inconsistent with an assumption of unimolecular adsorbed films on surfaces the adsorptive capacity of whose constituent elements is invariable. Hirst and Rideal recognised this and suggested that multimolecular layers of the polar molecules of carbon monoxide might be formed. This represents a return to Bodenstein's original point of view. Such is not necessary. The experimental results are consistent with the assumption of a surface of variable adsorptive capacity, the fraction of which capable of retaining adsorbed molecules for measurable intervals of time varying with the gas. On such a view, a copper surface at saturation with hydrogen is relatively bare as compared with the same surface saturated with carbon monoxide.

Varying Saturation Ratio for Adsorbed Gases on Different Preparations of the Same Catalyst.—To illustrate this point the data of Hirst and Rideal may be compared with similar data obtained by Pease[3]. In both cases saturation of copper surfaces with hydrogen and carbon monoxide was observed. In Hirst and Rideal's case, the ratio α_{CO}/α_{H_2} was 8.5. In Pease's case, the ratio was 2.86. Such a variable ratio with different preparations is quite inconsistent with an adsorbing surface of uniform adsorption capacity of the constituent units. It demands the assumption of varying capacity of the constituent units, differing with variation in the mode of preparation.

---

[1] J. Chem. Soc., **125**, 685, 694 (1924).

[2] J. Chem. Soc., **127**, 73 (1925).

[3] J. Am. Chem. Soc., **45**, 2296 (1923).

Varying Saturation Ratio on a Catalyst before and after Heat Treatment.—Numerous examples in the Princeton work show that not only is the variable ratio secured by variation in the method of preparation but it may also be secured by heat treatment of a catalyst after the initial determination of the adsorption ratio. Thus, in the case of a copper catalyst adsorbing carbon monoxide and hydrogen, the effect of moderate heat treatment is to diminish the saturation capacity, the diminution being proportionately greater with the hydrogen, the less strongly adsorbed gas. It is evident therefore that the saturation ratio α_{CO}/α_{H_2} will increase with heat treatment of the catalyst—a further index of varying adsorption capacity of constituent units of such a surface.

Varying Saturation Ratio on a Catalyst before and after Poisoning.—The same is true when the treatment involves poisoning. Thus, Pease[1] showed that poisoning a copper catalyst with mercury changed the saturation ratio α_{CO}/α_{H_2} from 2.86 to 19 a change in the same direction as is produced by heat, and a further evidence of a composite as opposed to a uniform surface.

Poisoning and Catalytic Reaction Velocity.—Were the catalyst surface uniform, a poison would produce an effect on reaction velocity proportionate to the surface it covers. Pease and Stewart have shown[2] that this is not the case. Adsorption of 0.03 cc. of carbon monoxide on a copper catalyst capable of adsorbing 1.0 cc. of hydrogen at 1 mm. gas pressure reduced the rate of hydrogenation, not by 3 per cent, as the extent of adsorption would indicate, but by more than 90 per cent. The conclusion seems inevitable that the portions of the surface capable of adsorbing hydrogen are not all equally effective in promoting hydrogenation. Only a small fraction of the surface is relatively efficient in this reaction.

Progressive Poisoning.—Inequality in the catalytic efficiency of surface atoms at once suggests that control may be exercised on the catalyst whereby its activity may be suppressed in stages. This has actually been achieved in a research by Vavon and Husson[3] on progressive poisoning. They found that the hydrogenation of propyl ketone by colloidal platinum could be suppressed by the addition of a limited amount of carbon disulphide. The poisoned catalyst would, however, still effect the hydrogenation of both piperonal and nitrobenzene. A further addition of the poison in limited amount suppressed the activity of the catalyst in the hydrogenation of piperonal but not in that of nitrobenzene. Finally, with a large amount of poison, the remaining reaction with nitrobenzene can be stopped. One other combination of hydrogenation reactions was studied. Such evidence inevitably demands the assumption of a catalyst surface the catalytic activity of whose component parts is not uniform. The following theory of the catalytic surface may therefore be offered.

---

[1] loc. cit.

[2] J. Am. Chem. Soc., **47**, 1235 (1925).

[3] Compt. rend., **175**, 277 (1922).

A Theory of the Catalyst Surface of Variable Activity.—The X-ray examination of metallic hydrogenation catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material. A granule of such a catalyst must, therefore, possess, in part, the ordered arrangement of the atoms found in crystalline material. The method of preparation of active materials suggests, nevertheless, that the ordered arrangement of the atoms has not been completely attained and that, here and there, on the surface of a partially crystalline material there are groups of atoms in which the process of crystallization is not yet complete.

The atoms in the plane surface of any face of the crystal, e.g., a face-centered cubic crystal of nickel, will be practically saturated by the neighbouring metal atoms in three dimensions, with the exception that there will be a certain degree of unsaturation towards the gas phase. In a sufficiently large plane surface of this type each atom will be identical in properties with the great majority of the others in the surface. There will be a certain variability in the surface fields of attraction with variation in the exposed face. The fields will be weakest in the closest packed faces, i.e., the 111 faces, stronger in the 100 faces and strongest in the 110 faces. Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surface, by reason of the fact that they are to a less degree surrounded by nickel atoms. For this reason they will possess stronger attractive forces for impinging atoms. Evidence for this is available in a study by Volmer and Estermann[1] of the growth of mercury crystals from the vapor. The crystals grow in the form of thin hexagonal leaflets the thickness of which is of the order of 1×10^{-4} of the hexagonal face. From a quantitative analysis of the experimental observations Volmer concludes that molecules condensing on the face of the leaflets are held temporarily in the force field of the surface, retaining, however, their motion until they either (1) evaporate or (2) are attracted to, and held at, the edges of the surface or (3) through contact with other molecules form the nucleus of another lattice layer. This latter alternative only becomes important when the plates, by growth of the edges, have attained a length and breadth of 0.3 mm. This increased attractive force at an edge will be surpassed by that obtaining at a corner. In the incompletely ordered atoms the attractive force will progressively increase as the degree of saturation by neighbouring nickel atoms becomes less and less, until, finally, in atoms which are only held to the granule by one attachment e.g. Ni-Ni, the unsaturation of the metal atom and the attractive force for impinging molecules will become a maximum. The methods of preparation of active catalysts and the activation of inactive masses all tend to produce arrangements of atoms in which these varying characteristics are multiplied.

---

[1] Z. Physik, **5**, 31, 188 (1921); **7**, 1, 13 (1921); Z. physik. Chem., **102**, 267 (1922).

It is at once evident how this view of the composite nature of a catalyst surface is in harmony with the observations already made as to the adsorption characteristics of such catalysts. For, the ratio of faces to edges to corners and to extra-lattice atoms will vary with varying preparations and with heat treatment. The attractive force of a surface atom may be adequate to retain one gaseous molecule, whereas another gas would suffer a practically completely elastic collision. The less saturated atoms in the catalyst surface will be the preferred positions of attachment of catalyst poisons. Hence, the varying ratio of adsorption between poisoned and unpoisoned catalyst. Hence, also, a mechanism for progressive poisoning.

The present concept of the composite catalyst surface is more embracing than that stressed by Langmuir[1] in dealing with the problem of catalyst activation. Langmuir emphasises that the distribution of catalyst atoms more or less at random will 'vary the distances between adjacent adsorbed molecules over wide range and some of these distances will be exactly right for the reaction to occur at the highest possible speed'. Variation in the distances between catalyst atoms, otherwise identical, does not appear to be adequate to account for *all* the variations in adsorption characteristics of single gases recorded in preceding paragraphs. The present concept substitutes for varying atomic distances varying degrees of saturation of surface atoms, from those in a plane surface to those held to the surface by a single atom-atom linkage. With this varying degree of saturation in the lattice structure comes not only the varying attractions for impinging molecules but also a varying chemical reactivity. For, the outermost atoms of the catalyst granule, linked by a single bond to the solid mass, are the atoms of a solid body most closely resembling the gaseous molecule. Now, a gaseous nickel atom can attach to itself four molecules of carbon monoxide to form nickel carbonyl. It does not seem improbable, therefore, that the outermost singly-linked nickel atoms shall be able to take up three molecules of carbon monoxide, or three molecules the linkage of which to nickel is that obtaining between the metal and carbon monoxide. The possibility thus arises of both hydrogen and unsaturated body being attached to the same nickel atom in a single complex at a catalyst surface, thus ensuring a more intimate electronic association than could be secured by adsorption on adjacent catalyst atoms.

Independent Evidence for the Theory.—The theory of a catalytic surface which has been put forward is thus far an *ad hoc* hypothesis designed to fit more of the experimental facts now known than is possible with preceding theories. Experimental evidence that unsaturation of the surface such as has been postulated does exist would strengthen considerably its probability. Such evidence appears to be available from a recent research. Garner and Blench[2] have recently published data on the heat of adsorption of oxygen on charcoal. They have obtained values ranging from 50,000 calories at ordinary temperatures to the astonishing value of 224,000 calories at low pressures and

---

[1] Trans. Faraday Soc., **17**, 618 (1922).

[2] J. Chem. Soc., **125**, 1288 (1924).

450°C. The astonishing nature of this latter value is at once evident when it is remembered that the heat of combustion of solid carbon to gaseous carbon dioxide is only 94,000-97,000 calories. The heat of adsorption may therefore be more than twice as great as the heat of combustion of the solid body.

It is at once evident that on the basis of the theory put forward in the preceding section this high value is to be expected. The high value recorded would represent the heat effect produced by the interaction of oxygen with the atoms of carbon most detached from the main mass of the solid carbon. The process occurring will be intermediate between the interaction of gaseous carbon and oxygen in which no carbon linkages are broken and that of solid carbon and oxygen in which four carbon-carbon linkages are broken in the oxidation process. The combination of gaseous carbon and oxygen involves the abnormally high heat effect of 350,000 calories owing to the high heat of vaporisation of carbon or alternatively to the endothermic breaking of the carbon-carbon linkage[1]. The value obtained by Blench and Garner is intermediate between the values for the combustion of the solid and the gaseous forms, and constitutes experimental evidence for the existence of isolated extra-lattice atoms.

Further Consequences of the Theory.—From considerations similar to those just advanced it follows that the thermal data for materials having a high ratio of surface to mass should be of greater magnitude than those obtained with coarsely crystalline material. Bäckström in some unpublished calorimetric work has shown that finely ground Iceland spar has a higher heat of reaction with dilute acid than the coarsely crystalline material. Ray[2] found that the heat of solution in hydrofluoric acid of finely ground crystalline quartz was higher than that of the coarse crystals. Material smaller than 200-mesh evolved 32.46 kg. cals. as opposed to 30.3 kg. cals. for the coarse material. The greater solubility of finely divided materials such as barium sulphate indicates also a higher heat of solution of finely divided, as compared with coarsely crystalline, materials. It suggests that charcoal should have a higher heat of combustion than the more perfectly crystalline graphite. This is actually recorded in the literature, a value of 97000 calories as opposed to 94000 calories for graphite being obtained. Uncertainty has attached to the former figure owing to the difficulty of purification. But, on the basis of the present theory a definitely higher value should be obtained for charcoal and for all other materials in which the process of crystallization is not complete. Thus, the heat of oxidation of active catalytic copper or nickel in the incompletely crystalline condition here postulated should be definitely greater than that of coarsely crystalline metal. An attempt to establish this experimentally is being undertaken.

It is evident also that the initial rate of evaporation of such active catalytic metals should be greater than those of the bulk material, since the more unsaturated the atoms in the lattice, the greater should be their freedom in escaping into the vapor phase. This is in agreement with the high thermal sensitivity of active metal catalysts, their sintering at relatively low temperatures. It does not seem impossible that the vapor pressures of these materials may be actually determined. Furthermore, the theory leads to a semi-quantitative formulation of the sintering process which will be discussed in a later section.

---

[1] Fajans: Verh. physik. Ges., **14**, 324 (1912).

[2] Ray: Proc. Roy. Soc., **101A**, 509 (1922).

The actual influence of the state of division on the properties of a material becomes much more pronounced when we come to deal with substances subject to dissociation. Thus, for example, taking the case of a dissociating oxide such as manganese dioxide, it seems fairly evident that the ease with which the oxygen is given up by the oxide will depend to a large extent on the degree to which the material is in the ordered arrangement of the large crystal. With the various methods of preparation at low temperatures of extremely finely divided manganese dioxide it would be expected that a very considerable proportion of the oxide ions would be found in corners, edges, or filamentary projections of material. These oxide ions should show an abnormal tendency to split off from their neighbouring ions as they are in less constraint than the atoms in the surfaces or interior of a larger crystal. In other words such finely divided material should show an abnormally high dissociation pressure of the oxide, as compared with that of the coarser crystals. That this is experimentally realisable appears to be substantiated by the report of Whitsell and Frazer[1] on the properties of active manganese dioxide such as is used in Hopcalite preparations. Whitsell and Frazer note that "the loss of oxygen by such manganese dioxide is noticed even at room temperatures and in a wet sample, indicating a dissociation pressure of oxygen in the pure manganese dioxide *greater than the partial pressure of the oxygen in the atmosphere.*"[2] They record, also, that English[3] has found that "these oxides behave as solid solutions, the oxygen pressure varying with the composition of the mixture." This is exactly what would be expected of a manganese dioxide which is losing oxygen, first from exposed oxide ions and then less and less readily from the ions more and more saturated by ionic neighbours. The discrepancy between Whitsell and Frazer's observation of a manganese dioxide with a dissociation pressure, at room temperatures, greater than 150 mm. and that of Askenasy and Klonowsky[4], who found a dissociation pressure of 23 mm. at 382°C. is in entire agreement with the demands of this present theory of the nature of such active materials. It accounts for the exceptional oxidation activity of such oxides.

This concept of a dissociation pressure varying with particle size recalls immediately the results obtained by Kendall and Fuchs[5] on the dissociation of various mixtures of oxides. These authors established undoubtedly the accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides. They claimed that the added oxide influences the dissociation pressure of the oxide. The present theory indicates in what manner the addition of oxides might promote increased dissociation pressure of the oxide. If the addition resulted, in effect, in a finer particle size by interspersing the added oxide more or less molecularly among the dissociating oxide an increased dissociation pressure should result. Their studies, therefore, merit further attention.

---

[1] J. Am. Chem. Soc., **38**, 807 (1916).

[2] Italics are the present author's.

[3] Dissertation, John Hopkins University.

[4] Z. Elektrochem., **16**, 104 (1910).

[5] J. Am. Chem. Soc., **43**, 2017 (1921).

There is already a definite amount of evidence that the interspersal of one oxide in another very definitely alters the speed with which the latter can be reduced. Thus, as the Dewar-Liebmann patent[1] indicates, the presence of ten percent of copper oxide in nickel oxide very materially lowers the temperature at which reduction of the nickel oxide can occur. This patent claim was very thoroughly studied by Armstrong and Hilditch[2], who point out that "in order to obtain the reduction of the nickel at the relatively low temperature, the copper and nickel must, prior to reduction be intimately and chemically associated with each other. Simple grinding of nickel and copper compounds is of little use; to secure the effect the latter must be precipitated together before reduction." It is very evident that this latter conclusion is that which would be suggested by the present theory, in which smallness of particle size, brought about by intermixture of crystal lattices, would lead to higher reactivity.

A more striking example of this effect is to be noted in the recent patent literature. A patent to the Badische Anilin und Soda-Fabrik[3] indicates that, in the reduction of mixtures of copper oxide and zinc oxide, the reduction of copper oxide is always accompanied by simultaneous reduction of some of the zinc oxide, the more the greater the percentage of copper. The writer has made a brief test of this point and finds that in equimolar coprecipitated oxides of copper and zinc some reduction of the zinc oxide occurs when the reduction of the copper oxide is affected at 300°C. This is a striking increase in activity over that of zinc oxide alone.

It is easy to see how the present theory unifies the various points of view concerning catalysis, representing, on the one hand, the intermediate compound theory with definite compound formation, through the borderline cases where only a fraction of the catalyst lattice undergoes change of the definite compound type to the extremest cases where only a very few atoms, the extra-lattice atoms, by virtue of the fact that they are unsaturated by neighbours, are capable of combining with impinging atoms or molecules, the catalyst atom or molecule complex then further reacting with the second reactant, the extra-lattice catalyst atom being thereby regenerated. The extent of the surface which is active will be determined by the reaction which is under study and will vary from case to case. Langmuir's evidence is unequivocal that practically every atom in the surface of platinum is active in certain circumstances in promoting the catalytic oxidation of carbon monoxide. The monoxide strikes oxygen held on the surface of the platinum. The same is not true, however, of the oxidation of hydrogen-oxygen mixtures on platinum where there is distinct evidence of activation of the metal accompanied by a roughening of the surface, that is, the production of extra-lattice atoms in the sense of the preceding theory. It is probably from the quantitative data of the poisoning of such activated catalysts that the surest evidence of such varied activity of surface atoms will be obtained. We shall consider this aspect in more detail in a later section.

---

[1] British Patent, 12981 (1913) and 15668 (1914).

[2] Proc. Roy. Soc., **102A**, 27 (1922).

[3] French Patent, 580905.

Armstrong and Hilditch[1] have suggested as a constructive extension of the preceding theory that the active atoms may be regarded as detached entirely from their association with the neighbouring metal atoms during the moment in which catalytic interchange is effected. The approximation of such extra-lattice atoms to the gaseous state suggests to Armstrong and Hilditch that the heat energy produced in the association of the reactants and catalyst atoms may suffice to effect this atom detachment. They thereby attain to a more definite conception of the "intermediate complex" of nickel, unsaturated body and hydrogen than they have previously been able to give. When the catalytic change is complete the nickel is again momentarily free and one of several things might happen:

I. The nickel atom might take part in further momentary unions with unsaturated molecules.

II. It might remain suspended as a nickel sol in the liquid.

III. It might become reattached to the solid surface.

In the last named case, with unsupported nickel, it would, by analogy with adsorption data, catalyst poisons etc., be supposed to migrate most easily to the most exposed portion of the surface, and a state of average similarity to the original catalyst would be maintained.

Armstrong and Hilditch find evidence in support of their suggestion in the presence of fine colloidal suspensions of nickel in hydrogenated oils and in the fine deposit of nickel found on the interior of iron or copper vessels used for the hydrogenation of liquids. They further cite the roughening of a relatively smooth platinum or other metallic surface during such processes as catalytic oxidation in a gaseous system as obvious evidence of the actual transference of atoms of the metal from one position of the surface to another.

Definite experimental evidence that such losses from platinum occur is evident from the early studies of Hulett and Berger[2] on the losses in weight from ordinary platinum foil and also from pure platinum when heated in air or in oxygen-containing gases. Table I records the results of successive heatings at two temperatures for periods of two hours each. The increased loss following the etching with aqua regia is especially to be noticed.

---

[1] Proc. Roy. Soc., **108A,** 111 (1925); Deuxième Conseil de l'Institut Solvay, April (1925).

[2] J. Am. Chem. Soc., **26,** 1513 (1904). See also Nahrwold: Wied. Ann., **35,** 116 (1888); Stewart: *ibid.*, **66,** 88 (1898); Holborn and Henning: Sitzungsber. Berlin Akad., **1902,** 936; **1903,** 245.

TABLE I

Platinum foil, 530 sq. cm. Heated in air.

Temperature	Time of heating	Loss in wt.	Remarks
900°C.	2 hours	1.6 mg.	
900	2 hours	1.4	
900	2 hours	0.9	
1020	2 hours	1.5	
——	——	220 mg.	Foil treated with aqua regia
1020	2 hours	5.6 mg.	

Burnishing with fine pumice had the same effect as treating with aqua regia. Pure platinum, as used in thermo-couple work showed the same effect. At 810°C. successive losses in 2 hours were 0.13 and 0.10 mg. At 870°C. the loss was 0.6 mg. in 2 hours. At 795°C. after aqua regia treatment, the loss was not measurable in 2.5 hours. Heated in vacuo or in oxygen-free atmospheres, no detectable losses were observed.

That the forces of adsorption are tremendously powerful in promoting the disintegration of solid bodies is very evident from the results of a recent research by Volmer and Mahnert[1] on the solution of solid bodies in liquid surfaces. In an effort to elucidate the well-known phenomenon of the erosion of camphor, partially immersed in water, at the water-air interface, Volmer and Mahnert have studied the mutual behavior of benzophenone and mercury surfaces. Benzophenone lowers the surface tension of mercury and is therefore adsorbed by the metal. By means of a micro-balance, these authors showed that a given solid sphere of benzophenone lost less than 1.5×10^{-7}g. per hour by evaporation in air. If the sphere were allowed to touch a surface of mercury, 20 cms. in area, for the space of one second, the loss in weight was 8×10^{-7}g. From this it is readily calculable that the surface of the mercury removes benzophenone from the solid sphere more than 18000 times more rapidly than this occurs by evaporation in air at the same temperature. From the vapor pressure at this temperature it can be also calculated that the loss by contact with a mercury surface is eight times more rapid than evaporation of the benzophenone into a perfect vacuum. The authors showed also, by an ingenious experiment, that the process occurring was not a solution process. Mercury was allowed to drop from a fine capillary in such a way that, at the moment of dropping, the mercury droplet touched a sphere of solid benzophenone. The mercury was collected in a vessel below. The total surface thus underwent a tremendous decrease which resulted in the excess benzophenone from the surface layers of the droplets collecting on the mercury surface in the larger vessel. It is evident therefore that the attractive forces operating between a mercury surface and solid benzophenone have the same influence traced out by Hulett and Berger in the platinum-oxygen case just considered, where the rate of evaporation was greater in the presence of oxygen than in a good vacuum. The same should be true for all metal-adsorption complexes such as are met in catalytic change.

---

[1] Z. physik. Chem., **115**, 239 (1925).

The fact that the extent of surface active in catalytic processes varies with the reaction catalysed militates against complete acceptance of the Armstrong-Hilditch standpoint, since it is difficult to believe that, in readily catalysed reactions, where practically the whole surface is active, any such detachment of atoms is involved. In certain cases, it is possible to see the reaction occurring on the surface, as, for example, in the manufacture of formaldehyde from methyl alcohol where the alternative oxidation and reduction of the copper catalyst is revealed by the constant colour change. Nor does it seem likely, with reactions catalysed by the platinum metals in the form of sols at ordinary temperatures, that the loss of atoms from the catalyst surface is involved. The same applies also to the case of the refractory oxides acting as catalysts. Armstrong and Hilditch believe that the exothermic nature of the reactions should result in a progressive devaluation of the catalyst in consequence of a series of localised exposures to high temperatures. They have never observed this, probably because their work has been mainly with supported catalysts raised to moderate temperatures before use. With unsupported catalysts, however, such progressive devaluation as a result of reaction has been well established by Russell[1], who showed that an unsupported nickel catalyst reduced at 250°, underwent steady deterioration when used for catalysis of hydrogen-carbon monoxide mixtures in the temperature range 200-260°C.. When, however, the catalyst was heat-treated at 400°C. no further loss in activity was noted by catalysis in the lower temperature range.

Larson and Smith[2] have shown, contrary to the opinion expressed earlier by Pease and Taylor, that the catalytic oxidation of hydrogen on nickel surfaces involves exactly the same behavior as in the case of the copper catalyst. "The experiments indicate that two distinct reactions take place during the catalytic formation of water on nickel and copper. One of these reactions involves the formation of an oxide that is not readily reduced by hydrogen if oxygen be present. During the synthesis, therefore, the reduction of this oxide probably contributes little to the total water being formed. The other reaction is most in evidence during the initial period of high activity. It is undoubtedly the faster reaction and as such accounts for the greater part of the water formed, not only initially but also during the period of low activity."

These results indicate very definitely that in the early stage of the catalysis at the lower temperatures and probably indefinitely at the higher temperatures the whole of the nickel or copper surfaces has catalytic activity and that this is poisoned by oxide formation. On the basis of the ideas put forward in the preceding theory the reactivity of adsorbed oxygen or oxide ions with hydrogen will be the greater the more isolated they are from one another. We can therefore picture the fast reaction as occurring between isolated adsorbed oxygen or oxide ions and impinging hydrogen molecules or with hydrogen atoms or molecules. The chance that such individual groupings will grow into a film of oxide will be progressively less as the temperature is raised. This is in accord with the experimental facts. As Larson and Smith point out, the phenomena of ammonia synthesis parallel the hydrogen-oxygen case just discussed, a film of nitride acting to retard reaction. In such case a similar mechanism would hold for the synthesis process, namely reaction of impinging hydrogen molecules or adsorbed hydrogen with isolated adsorbed nitrogens.

---

[1] J. Phys. Chem., 29, 1325 (1925).

[2] J. Am. Chem. Soc., 47, 346 (1925).

Promoter Action

In the Third Report the experimental data of Medsforth[1] and of Armstrong and Hilditch[2] on the promotion of nickel catalysts for methanation and for the hydrogenation of ethylenic compounds were presented. In the former paper Medsforth stressed a specific dehydration effect of the promoter, while, in the latter, promotion was attributed to extension of available catalyst surface. This clear-cut case of divergence was capable of test experimentally and this test has been carried out by Russell and Taylor[3]. An investigation was made of the action of thoria on nickel supported on pumice, in catalysing the interaction of carbon dioxide and hydrogen to form methane and water. Reaction velocities and extent of surface as measured by adsorption were studied on the same catalyst preparation. The experimental work on such supported catalysts shows that no proportionate increase in adsorption accompanies the activity shown by the promoted catalyst. It therefore appears that the surface of the catalyst has undergone a qualitative rather than a quantitative change. The actual experimental figures show that, whereas the promoted catalyst (Ni, ten per cent thoria on pumice) effects a given percentage reaction at a ten-fold increase in velocity over the non-promoted catalyst (Ni on pumice), the extension of surface as measured by adsorption of either the carbon dioxide or the hydrogen at reaction temperature only undergoes a twenty per cent increase. The harmony between this conclusion and the general considerations already put forward concerning the nature of the catalyst surface is at once evident. Even if it be assumed that the whole of the nickel surface capable of adsorbing hydrogen were catalytically active in the case of the promoted nickel catalyst, it would follow that not more than 10-12 per cent of the surface of the unpromoted catalyst surface adsorbing hydrogen would have any catalytic activity.

That such a percentage of active surface is only an upper limit, can be illustrated by an instructive calculation from the data of Medsforth. He found that a concentration of 0.5 per cent ceria in the nickel catalyst causes a ten-fold increase in reaction rate. Assuming uniform distribution of promoter in the catalyst, this represents one molecule of ceria in every 1130 atoms of nickel in the catalyst surface. This minute change in surface concentration brings about a ten-fold increase in catalytic activity. This strongly suggests that in an unpromoted nickel catalyst the active nickel atoms are of the order of 1 in 11300 atoms. It should be noted that this represents a lower limit, since uniformity of distribution is assumed. Nevertheless it exhibits a state of affairs concordant with the data already set forth on the quantitative aspects of poisoning and on the theory of the catalytic surface generally.

---

[1] J. Chem. Soc., **123**, 1452 (1923).
[2] Proc. Roy. Soc., **103A**, 586 (1923).
[3] J. Phys. Chem., **29**, 1325 (1925).

In the case of unsupported catalysts the thoria acts not only as a promoter but also as a support to increase the extent of surface. This increase in extent of surface is shown by its increased adsorption values and by the greater apparent volume of the catalyst, its resistance to heat treatment. Russell's experimental results also show a specific action of thoria in increasing the relative amount of carbon dioxide adsorbed. A study by Hirst and Rideal of the promoter action of palladium on copper[1] also indicates an adjustment of ratio of adsorbed gases as well as the importance of the metal-promoter interface.

If a copper catalyst be promoted with small quantities of palladium and the ratio carbon monoxide to hydrogen determined for a series of such promoted catalysts, one of the following results may be anticipated: If the palladium causes no specific effect beyond a surface extension, the ratio $CO:H_2$ consumed will remain unaltered: alternatively, if promoting action is in reality an additive effect, then the $CO:H_2$ ratio will decrease with increasing palladium concentration and the ratio should be capable of accurate calculation from both the known ratios of $CO:H_2$ for the copper and the palladium each in the pure state and from the stoichiometric composition of the catalyst. If, on the other hand, the addition of small quantities of palladium promotes the activity of the oxidised copper for carbon monoxide, we should anticipate a higher $CO:H_2$ ratio for small additions of palladium, rising to a maximum with subsequent increase in the palladium concentration and finally falling to a $H_2:CO$ ratio higher than that for pure palladium at those concentrations where addition of copper promotes the palladium.

Hirst and Rideal found that small quantities of palladium, up to 1.70 per cent, increase the ratio of $CO:H_2$ burnt at any particular temperature in presence of a copper catalyst. A maximum occurs on the addition of 0.20 per cent. A promoted catalyst containing 1.70 per cent of palladium yields the same ratio as pure copper. Catalysts containing more than 1.70 per cent palladium yield a lower $CO:H_2$ ratio than copper, but higher than palladium. This increase in the ratio of $CO:H_2$ burnt on addition of small amounts of palladium is contrary to that which would be expected, as outlined in the preceding paragraph, either on the basis of extension of surface or of dilution of the catalyst surface with palladium. The result obtained is to be anticipated, however, if the reactivity of the oxidised copper at junctions such as Cu. Pd is affected.

To elucidate further the mechanism of the promoter action, Hirst and Rideal[2] studied the adsorption of hydrogen and carbon monoxide singly and in various mixtures of copper, palladium and promoted catalysts. They conclude that the addition of palladium to copper produces an increase in the carbon monoxide adsorption and a decrease in the hydrogen adsorption as well as a relative increase in the carbon monoxide of the adsorbed phase in the presence of both gases. The relative increase in the adsorption of carbon monoxide was found to be in good agreement with the relative increase in the ratio $CO:H_2$ consumed in the catalytic combustion process. The specificity of the effect on adsorption produced by the palladium promoter is further evidence that the promoter action is not merely due to surface extension but involves the further factor of the nature of the interface between catalyst and promoter.

---

[1] J. Chem. Soc., **125**, 685 (1924).

[2] J. Chem. Soc., **125**, 694 (1924).

It is desirable to insist that these results do not exclude the possibility that, in addition to the several effects already discussed in connection with the function of the promoter, a promoter may also act by activating one of the reaction species. There is as yet no published evidence of any such case unequivocally demonstrated but there are several cases where it may exist. No evidence is yet forthcoming as to the mechanism whereby nitrogen is activated in the synthesis of ammonia from the elements. Some data by Taylor and Marshall[1], show that activation of the hydrogen alone as, for example, by excited mercury atoms, is not sufficient to bring about ammonia synthesis; whereas this is sufficient to cause reaction with ethylene and carbon monoxide. Certain of the promoters in ammonia-making catalysts may effect nitrogen activation, although with some, qualitative change in the surface of the catalyst by the added promoter is adequate to account for observed effects. It is possible that some information on this point may be achieved from the data on the heats of adsorption.

Larson and Smith, in the paper already cited, point out a further possible function of the promoter. They indicate that the addition of certain promoters decreases the amount or stability of the nitride accumulation, the result being a more reactive catalyst. This is in harmony with the concept that isolated molecular units have a higher reactivity than the material in bulk. The promoter in such case would act to isolate small units of the catalyst material giving them thereby enhanced reactivity, securing, in another manner, for the catalyst preparation, the advantages accruing from fineness of division.

The divergences between different substances used as promoters has also to be accounted for in any complete theory. It is apparent that the properties of the promoter used will in part determine its distribution in the catalyst, since solubility is one of the important factors which will determine the time of separation. Its lattice as compared with that of the lattice of the compound from which the catalyst is prepared will also affect distribution.[2] Many more experimental data are required on such points.

---

[1] J. Phys. Chem. **29**, 1140 (1925).

[2] Concerning this point see Wyckoff and Crittenden: J. Am. Chem. Soc., **47**, 2866 (1925).

One other aspect of the problem of promoters should also be placed on record. Considerable discussion of the reason for the desirability of oxygen in hydrogenation processes, especially at finely divided platinum surfaces in liquid systems, has taken place in the last few years. There are indications that a clue to the real cause has emerged from the studies of Adams and Carothers[1] on promoted platinum catalysts. They have shown that the reduction of benzaldehyde in presence of platinum is rapidly suppressed when pure platinum is used. They showed, however, that the presence of a very small amount of ferrous chloride enormously accelerates the platinum catalysis and that no reduction of activity is observed over considerable periods of reaction time. Their most recent paper supplements the list of promoters extensively, thirty-six other inorganic salts than iron having been studied with positive effects from many, including manganese, nickel, cobalt, zinc, copper and uranium salts. All alkalis accelerated the reaction. Mineral acids had little effect. Carothers and Adams now reject their earlier hypothesis, which was also that of Willstätter and Waldschmidt-Leitz, that the aldehyde deprived the platinum of the oxygen that is essential to its activity. They now believe that the most consistent explanation of the observed retardation with pure platinum is to be based on strong or irreversible adsorption of the aldehyde by the platinum. The utility of manganese, iron and nickel salts as promoters, themselves familiar as powerful oxidation catalysts, makes it improbable that they would, under the conditions of the experiment, have the opposite effect on the oxidation of the aldehyde associated with the platinum. The function of the oxygen as a regenerator would thus be to burn off strongly adsorbed aldehyde. With a promoted catalyst there should consequently be a better opportunity for both reactants to be present in favorable configuration on the catalyst surface. With pure platinum, the aldehyde is assumed by Adams and Carothers to be a self-poison, and the function of the promoter is in some way to bring about a desorption of the aldehyde and so permit a renewal of the platinum surface.

It should be borne in mind, however, that this is not the only possibility as regards self-poisoning of the surface although it appears at first to be the most plausible. There is a possibility that it is the hydrogen that is the self-poison and the arguments advanced above would hold almost equally well. It would account, moreover, for the adverse effects of pre-treatment with hydrogen in a number of other reactions earlier discussed[2]. This point of view is confirmed by a recent research of Kab[3] in Bredig's Laboratory. He shows that the activity of platinum black prepared by the method of electrical disintegration is conditioned by the gas in which it is prepared. If prepared in hydrogen it is quite inactive in the decomposition of formic acid to carbon dioxide and hydrogen. The removal, by continued evacuation, of hydrogen from the preparation is in itself an activation; treatment with oxygen, Kab finds, is not necessary though an available method of removing hydrogen. Carbon monoxide behaves like hydrogen. Disintegration in an oxygen atmosphere yields an inactive catalyst. Treatment, with oxygen, of an inactivated catalyst was shown to result in the removal of hydrogen with corresponding activation.

---

[1] J. Am. Chem. Soc., **45**, 1071 (1923); **46**, 1675 (1924); **47**, 1047 (1925).

[2] Second Report, p. 814 et seq.,

[3] Z. physik. Chem., **115**, 224 (1925). See also, Beans and Hammett: J. Am. Chem. Soc., **47**, 1215 (1925).

Promoter action, in such cases, where one of the reaction constituents acts as a self-poison, could therefore be ascribed to the effect of the promoter in altering the ratio of reactants adsorbed, a point of view originally suggested by Rideal and Taylor[1], some quantitative evidence for which has been obtained by Russell with promoted, unsupported nickel catalysts in the research already discussed.

The Effect of Heat Treatment of Catalysts

It is possible, with the aid of the concept of the catalytic surface which has been developed to proceed to a semi-quantitative treatment of the phenomenon of sintering accompanied by loss of adsorptive capacity and reactivity on the part of the catalyst material[2]. The data of Pease on the effect of heating copper catalysts to successively higher temperatures was discussed in the preceding Report. They were characterised by the fact that "for each rise in temperature a noticeable decrease in activity occurred but further heating at the same temperature was without marked effect. There seems to be a stable condition of the surface corresponding to the highest temperature to which it has been heated." Russell has shown the same to hold true for both unsupported nickel and promoted unsupported nickel.

In a composite metal catalyst surface with atoms ranging in saturation from those almost completely saturated by surrounding atoms to those only held to the solid surface by a single metal-metal linkage, there will be a whole range of corresponding energy quantities, the heats of evaporation of individual atoms from the surface. These heats will increase as the atom becomes more saturated with neighbouring atoms and the increase will be approximately proportional to the number of atoms to which the given atom is attached. Thus, if Q be the heat of evaporation of a singly linked atom, 2Q will be that of a doubly linked atom and so on. Now, from the Boltzmann equation, the rate of evaporation will be proportional, for a singly linked atom, to the quantity, $e^{-Q/RT}$ and for a doubly linked atom, to the quantity, $e^{-2Q/RT}$ and so on. It is therefore evident that the rate of evaporation will fall off exponentially as the number of atom linkages increases. Thus, to cite an actual example, let us assume that Q for a single linkage has a value of 5000 calories and the sintering temperature T is 500°K. it is evident that the rate of evaporation of singly linked atoms will be proportional to $e^{\frac{-5000}{2\times 500}}$ or e^{-5}. For doubly linked atoms the rate will be proportional to e^{-10}. The rates of evaporation will therefore be in the ratio of $e^5 : 1$ or $148.4 : 1$; in other words, at a temperature at which singly linked atoms leave the surface freely, doubly linked atoms are practically non-volatile. The relative rates for singly, doubly and trebly linked atoms will be $22046 : 148.4 : 1$.

---

[1] "Catalysis in Theory and Practice," page 31, (1919).

[2] I am indebted to Dr. Langmuir for the suggestion of this approach to the problem of sintering.

Herein lies the reason for the extraordinary temperature sensitivity of active catalytic agents, not only to the subsequent heat treatment but also to the thermal effects accompanying preparation and reaction. This is alone adequate to account for the divergences in catalysts preparations obtained by Adkins and Lazier[1] by reduction of nickel oxide with alcohol and with hydrogen. Since the thermal effect in the case of alcohol is less than that with hydrogen by an amount equal to the heat of dehydrogenation of alcohol, 11500 cals.[2], it is evident that the active centers—the detached atoms of nickel are subjected in the alcohol case to far less severe thermal treatment than in the hydrogen reduction. A more active surface, therefore, naturally results. The divergence is emphasised by the difference in speeds of reduction. With ethyl alcohol some sixty minutes are only required, as compared with twelve hours at the same temperature with hydrogen. When first used, therefore, marked divergences of efficiency are revealed. These are, however, not differences in "type" but differences in the atom linkage of the surface atoms. That such differences are of the most fundamental importance is very strikingly illustrated by some new work of Pease and Purdum[3], in which the lowering of the temperature of reduction of a sample of copper oxide from 200° to 150°C. made a product at the lower temperatures with which benzene could be hydrogenated whereas that prepared at the higher temperature was quite incapable of reducing the benzene nucleus. Failure to observe this accounts for Sabatier's[4] emphatic statement that benzene cannot be hydrogenated in presence of copper. Russell has shown that the heat of reaction alone is sufficient to cause a deterioration in the catalytic activity of an unsupported nickel catalyst prepared by reduction at 250°C. even though the working temperature, as measured by a thermometer bulb embedded in the catalyst mixture, never exceeded 265°C. Successive experiments between 200° and 250°C. showed steadily decrements in activity. An initial activity of fifty per cent methane formation at 225°C. fell to twenty per cent conversion when the catalyst had been used for 25 hours between 200° and 250°C.

It is the extra lattice atoms which possess the abnormal adsorptive power and abnormal volatility. This latter is well indicated by Langmuir's observation that a film of molybdenum vaporised on to a glass surface cooled in liquid air undergoes an irreversible change on warming to room temperature; that is, crystallisation is occurring, some 2500° below the melting point of the massive metal. The loss in adsorptive power has already been discussed.

---

[1] J. Am. Chem. Soc., **46**, 2291 (1924).

[2] Rideal: Proc. Roy. Soc., **99A**, 153 (1921).

[3] J. Am. Chem. Soc., **47**, 1435 (1925).

[4] Sabatier-Reid: "Catalysis in Organic Chemistry", 511, 522 (1922).

Specific Activation

The preceding sections attempt to give a conception of the catalyst surface which is consistent with the physical and chemical properties of such a surface and with independent observations from experimental work outside the immediate domain of catalysis. As was pointed out, however, in the Second Report, the effect of a catalyst does not depend exclusively on the increased concentration due to the attractive forces at the catalyst surface; all agree that the effect of the catalyst is specific. The problem of the specificity still remains to be solved.

In perhaps one direction, progress towards a solution of the problem may be definitely claimed. One feature of specificity which has been much stressed is that a given hydrogenation process may be effected with one hydrogenation catalyst but not with another. A good example of this type has been the hydrogenation of benzene. Sabatier was quite emphatic that hydrogenation of the benzene nucleus was not possible with a copper catalyst, but proceeded rapidly and smoothly with nickel. The research of Pease and Purdum already cited shows that the emphasis was unfounded since, with copper, hexahydrobenzene may be secured, though with less efficiency than with nickel. From the details of Pease and Purdum's results, some clue as to the cause of this presumed specificity may be obtained. They showed that it was necessary carefully to control the preparation of the copper catalyst. Reduction of a copper oxide sample at 200°C. gave an inactive copper. Reduction of the same kind of copper oxide at 150°C. gave a copper with which a forty per cent conversion could be secured. Now this alteration in preparation, as the initial sections of this report indicate, will yield a catalyst material in which the proportions of extra-lattice atoms capable of adsorbing more than one reacting molecule will be increased; in addition, it has been shown that, in the catalyst so produced, the adsorption ratio $H_2 : C_6H_6$ will be increased (heat treatment of a catalyst decreases this ratio; see earlier sections). Preparation of the catalyst at lower temperatures will thus have two effects, both favorable to reaction on the assumption that, with an ordinary copper catalyst, hydrogenation does not occur since the surface is practically exclusively monopolized by benzene. Pease and Purdum reach this conclusion from other evidence. In other words, specificity of catalytic action may arise from the unsuitability of the adsorption ratio of the two reactant gases on one hydrogenation catalyst as compared with that on another, abundant kinetic material now existing to show that variation in adsorptive capacities is associated with variation in catalytic activity. This thought emphasizes anew the necessity for obtaining experimental data on the adsorption of gases by catalysts from mixtures of gases. There are very few such data. Some obtained by Hirst and Rideal[1] indicate a very strange behavior, the total adsorption being far less than would be anticipated on the basis of the law of mixtures. Their work should be repeated with more adsorptive samples and other pairs of gases should be studied.

---

[1] J. Chem. Soc., **125**, 694 (1924).

The idea that self-poisoning of the catalyst might account for specificity in the methanation process is also worth considering. On nickel, where methanation occurs readily, the adsorptions of hydrogen and carbon monoxide are comparable in magnitude. On copper, carbon monoxide is much more strongly and abundantly adsorbed than is hydrogen; and we might assume that the carbon monoxide poisons the methanation process on copper, especially in view of the fact, which the Pease-Stewart research[1] on ethylene-hydrogen combination in presence of carbon monoxide reveals, that, of the total adsorbing surface, only a very minute fraction is active in that reaction, a much more readily catalysed reaction than the methanation process. The disturbing aspect of this idea is, however, that there is marked specificity existing between nickel and copper, in the matter of the decomposition of carbon monoxide to carbon dioxide and carbon

$$2CO = CO_2 + C.$$

This reaction occurs readily with nickel and has not yet ever been observed by the writer even with quite active copper catalysts. Both adsorb carbon monoxide and there can hardly be a question of self-poisoning. But, we are so ignorant of mechanism even in a simple reaction of this kind that, as yet, there seems no satisfactory explanation available. Is this specificity to be associated with the ability to form carbonyl in the case of nickel and the absence of such compounds with copper? And if so, what is the difference between a carbon monoxide molecule adsorbed on a nickel surface and one on a copper surface? What methods are we to adopt to make clear such differentiations?

Dew and Taylor[2] have sought to establish such differentiation in the case of ammonia adsorbed on iron, nickel and copper, by determination of the heats of adsorption of ammonia on these metals at low partial pressures. The heat effect is greatest with iron and least with copper which is also the order of the catalytic efficiency of these metals in decomposing ammonia. But, it is not as yet clear what change in the molecule of ammonia is to be associated with these differences in the heat of adsorption.

That answers to such queries as those above might come from a study of the alternative decompositions of organic molecules has inspired a considerable amount of research in recent years, the substances studied including formic and other acids, alcohols, esters and amides. Many of the results of such studies have been included in the earlier reports. The most comprehensive studies have been those of Adkins and his co-workers[3], and these have led Adkins to what may be termed the 'spacing' theory of specific catalytic action.

Adkins found that the mixed dehydration and dehydrogenation of esters and of alcohols on alumina and titania surfaces was very sensitive to the nature of the catalyst material and the source from which it was obtained. From a study of the activities of aluminas and titanias prepared from salts, acids and alkoxides, Adkins has formulated a 'spacial theory' in which the spacing of the "active points" plays a fundamental part. This spacing is thought to be secured by choice of the starting material for the preparation of the catalyst, by changing the size of the radical (e.g., OEt) attached to the aluminium atom when the compound goes (by hydrolysis) into the solid state. As an *ad hoc* hypothesis it can be made to fit the experimental facts in the case of the two reactions noted with considerable success. His work supplies an experimental basis for the theory which, however, involves difficulties when it comes to the problem of the experimental facts of the adsorption of reactant gases, taken singly, and of poisoning (see page 167).

---

[1] J. Am. Chem. Soc., 47, 1235 (1925).

[2] Dew: Thesis, Princeton (1924).

[3] For literature references see 2nd Report and J. Am. Chem. Soc., 47, 807 (1925).

Apart from the inherent improbability, judging by recent X-ray studies, that the distances between the atoms, molecules or "active points" of the catalyst can be modified in such a manner as claimed by Adkins, especially when the high temperature of use is borne in mind, certain other data of Adkins are hard to reconcile with his spacing theory. Thus, he has observed that, although the reactions already mentioned are sensitive to this assumed spacing in aluminas, this is not all true for such similar reactions as the dehydration of amides to yield nitriles, the decomposition of acids to ketones and the catalytic removal of hydrogen halides from alkyl halides. Similarly, formic acid decomposition on titania is as rapid on an ignited as an unignited catalyst.

This divergent behavior in these last four cases, quite inexplicable on the "spacing" theory, is strongly reminiscent of reactions in other fields of catalytic work, readily catalysed by a surface of almost any low activity, as, for example, with metals in the reduction of nitrobenzene. It suggests that every atom in the surface possesses catalytic activity—Langmuir's original assumption. On this basis, the abnormal behavior in the cases of alcohols and esters would arise by reason of the fact that only a certain fraction of the surface atoms were active in the decomposition processes. If this were so, the reactions would show sensitivity to poisons such as we have already discussed. The most likely poisons for acidic catalysts of this type will obviously be basic materials. An examination was therefore undertaken of Adkins' abundant experimental material to ascertain how far there was internal evidence of the operation of basic materials as poisons. The evidence which this revealed was arresting. Briefly, one can say that Adkins' catalyst data can be reinterpreted on the basis of possible contamination with poisons principally alkaline or salt poisons. This is so, since, as Adkins observes, titania from tetra-ethyl titanate is very different in its catalytic activity from Demarçay's oxytitanates—a fact which Adkins did not expect. He observes, however, in his experimental data that "the wash water (in the preparations from certain oxytitanates) reacted alkaline to phenol phthalein showing that some occlusion of sodium ethoxide had taken place in the crystallisation". These oxytitanates yielded the catalysts in which the ratio of $C_nH_{2n}/(C_nH_{2n} + H_2)$ was a minimum, in which also the absolute activity was a minimum. Similarly, titania from sodium titanate gave a low ratio and a low absolute activity. In acetic acid decomposition these two were the most active. Furthermore, as evidence of sensitivity to poisoning, we may cite: "it has been found impossible to duplicate absolute activity in the preparation of certain catalysts." Charriou has shown[1] that the catalytic decomposition of ether by heating with alumina at 250°C., is inhibited if the alumina has adsorbed small amounts of other inactive substances. He showed that adsorbed lime was the most efficient of the inhibitors which he studied.

The most decisive evidence, however, that "spacing" is not the fundamental factor and that poisoning is, can also be cited from a recent paper of the Adkins series[2]. Bischoff and Adkins show that the decomposition of butanol at the titania surface, is modified profoundly by the presence of a basic agent in the gas phase, namely ammonia. They point out "an observation of no little importance," with titanias of two different "spacial" types, that the presence of the ammonia "materially altered the ratio of gaseous products, more butane and hydrogen and less butylene being formed. In fact, the effect of the ammonia was many times as great in shifting the reactions as was the equivalent of water." In other words, Adkins and Bischoff, here, by their own experiments prove that spacial distances between atoms, molecules or "active points" of the catalyst have no decisive influence on the ratio of reactions and that the presence of a poison does.

The concept of the solid catalytic surface developed in the earlier sections may therefore be utilised again to recast this concept of specific activity of catalytic materials. The surface is composite, with atoms, ions or molecules in the surface in varying degrees of lattice saturation. For some reactions, notably the decomposition of acids to yield ketones, amides to yield nitriles and alkyl halides to yield olefines and the corresponding hydrogen halides, the bulk of the surface atoms are to be considered active. For the decomposition of alcohols and esters, on the contrary, only a fraction of the surface and that, presumably, the less saturated lattice atoms, possesses catalytic activity sufficient to effect decomposition. The mode of decomposition and the nature of the products will, in such case, depend on the nature and arrangement of the extra-lattice atoms, which in turn will depend largely on the mode of preparation and subsequent treatment accorded to the catalyst. If such be true, it should follow, also, that the mode and extent of catalytic decomposition should be markedly sensitive to poisons in the case of alcohols and esters, and to a much less degree so sensitive for ketones, amides and alkyl halides. Alternative modes of decomposition would then be attributable to the differences in the molecular structure of the adsorbed reactant brought about by its attachment to the catalyst. What the nature of the changes in molecular structure so caused may be and the manner in which they may be established with certainty is not readily apparent. The possibility of their existence, however, is patent from observations on the effect of substituents, as for example, chloro and amino groups on the properties of organic fatty acids. In these cases, substitution at one end of a long hydrocarbon chain exercises a profound influence on the acidic property at the other end of the chain. For this reason also the chemical nature of the atoms or ions on which the reactant is adsorbed should also have a determining influence on the mode of reaction.

---

[1] Compt. rend., **180**, 213 (1925).

[2] Bischoff and Adkins: J. Am. Chem. Soc., **47**, 812 (1925).

That poisons do determine the path of reaction is already well known; poisoning may be well utilized to yield a preferred product, and to such cases the term beneficial poisoning has been applied. A very obvious application is in the case where a catalytic process proceeds too far with an active catalyst. By minimising the activity of such a catalyst or poisoning the more highly reactive patches with the requisite poison, the reaction may be stopped at the desired stage. Many investigations into the conditions necessary to secure a good yield of a desired product may, in reality, be unconscious applications of this procedure of beneficial poisoning. An example suggestive of this may be quoted.

Armstrong and Hilditch[1] have shown that in the catalytic dehydrogenation of ethyl alcohol in the presence of copper, the presence of water in the alcohol improves the yield of acetaldehyde relative to that of hydrogen. Thus, at 300°C., whereas anhydrous alcohol only gave an aldehyde–hydrogen ratio of 67 per cent, alcohol containing 8 percent water gave a 95 per cent ratio. With the anhydrous alcohol there is a marked increase in the yield of gaseous products, principally methane, carbon monoxide and carbon dioxide in addition to the hydrogen. It is evident that, with the anhydrous alcohol, secondary decomposition of aldehyde is much more pronounced than with alcohol containing water. Thus, methane and carbon monoxide result from one such secondary decomposition.

$$CH_3CHO \longrightarrow CH_4 + CO.$$

Evidently, the water acts as a beneficial poison in that it poisons the catalyst for such secondary decompositions which apparently require a large energy of activation, in all probability as a result of a strong preferential adsorption on the catalyst surface. Armstrong and Hilditch showed, by passing aldehyde vapor together with water over a copper catalyst, that the water had a considerable protective influence on the aldehyde.

The dehydrogenation of alcohol in the presence of nickel occurs at lower temperatures than in the presence of copper but the secondary decomposition is very high. The data of Armstrong and Hilditch show that dehydrogenation occurred at 250°C. The aldehyde-hydrogen ratio was only 35.7 per cent and the evolved gas contained 60 per cent hydrogen, 20 per cent carbon monoxide and 15-17 per cent methane. Evidently, in this case, the 8 per cent of water in the alcohol used was not sufficient to protect the aldehyde produced. It would be interesting to extend this study of dehydrogenation with nickel in the presence of water to see whether the secondary decomposition could be largely suppressed by increase of water content in the alcohol, since the low yields obtained with copper at the higher temperatures could be partially restored by such an increase in water content.

---

[1] Proc. Roy. Soc., **97A**, 262 (1920).

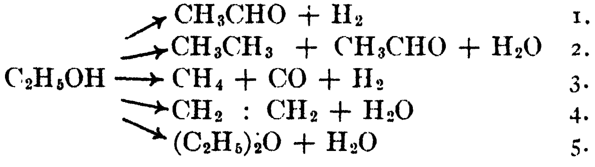
Palmer's study[1] of this same reaction in the presence of a copper catalyst indicates that alcohol itself plays the same role as the water in the experiments already cited. He showed that, below 300°C., the secondary products were negligible when the dehydrogenation of alcohol occurs; but, if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300°C., much of the aldehyde is decomposed. Bancroft has suggested that such cases might be called "protective poisoning".

The same procedure was used during the years 1917-1919 for the production of ethylene from alcohol in presence of kaolin. Instead of a low temperature process the reaction was conducted at red heat and the products were protected from decomposition by using alcohol-water mixtures, even though the process was dehydration. The researches of Rosenmund, Zetsche and Heise have been cited by Bancroft in an earlier report.

Recent work by Adams and his co-workers[2] indicates that the use of permanent poisons on the catalyst surface as well as temporary poisons in the gaseous reactants may also be used deliberately to direct a catalysis. Thus, with a platinum-iron catalyst, cinnamic aldehyde undergoes reduction to phenyl propyl alcohol. If the catalyst be suitably poisoned with zinc, the product is cinnamyl alcohol. The efficiency is very sensitive to the amount of zinc salt employed to poison the catalyst surface so that a question of the geometry of the platinum and zinc atoms in the surface as compared with that of cinnamic aldehyde may be involved in the explanation of the action of the poison. Armstrong and Hilditch see in such studies of selective hydrogenation a most promising field of research in heterogeneous catalysis[3].

Professor Adkins' comment on the point of view put forward in the preceding pages is worthy of record. "There appears to be little doubt that the atoms constituting the surface layers of a solid catalyst differ in the degree of their unsaturation. However, it is very doubtful if this fact, together with its resultant possibility of selective poisoning, offers any adequate explanation of the variations in ratios between simultaneous organic reactions, as studied in the Wisconsin Laboratory.

"In the case of ethanol there are at least five distinct reactions that take place at the surface of solid catalysts. The first four reactions take place over the same temperature range.



$$C_2H_5OH \left\{\begin{array}{lr} \nearrow CH_3CHO + H_2 & 1. \\ \nearrow CH_3CH_3 + CH_3CHO + H_2O & 2. \\ \longrightarrow CH_4 + CO + H_2 & 3. \\ \searrow CH_2 : CH_2 + H_2O & 4. \\ \searrow (C_2H_5)_2O + H_2O & 5. \end{array}\right.$$

The idea that Reaction 1 took place at the surface of those catalysts that strongly adsorbed hydrogen, and Reaction 4 with those catalysts that adsorbed water, is no longer held tenable even by its originator. The only other suggested mechanism is that the catalyst causes, through the formation of a compound with the ethanol, a rearrangement of the electrons within the alcohol molecule, so that a split in the molecule occurs. On the basis of this idea, (which is due to Langmuir) one may say that copper forms a compound with ethanol so that the aldehyde rearrangement is the easier, which the alumina-ethanol compound most readily rearranges to give the alkene. One has then assumed that there are two distinct types of compound, one of which is liable towards the dehydrogenation reaction and the other towards the dehydration. Both reactions occur simultaneously over zinc oxide, the proportions not being a characteristic of zinc oxide but of the zinc compound out of which the oxide is prepared. Are there then *two* zinc oxide-ethanol compounds, one liable towards dehydrogenation and the other towards dehydration? Are there four iron oxide ethanol compounds, for Reactions 1, 2, 3, and 4 taking place simultaneously over that catalyst? On the basis of Dr. Taylor's hypothesis, a slightly unsaturated surface atom might induce one reaction, a more unsaturated one another reaction, etc. That is to say an atom of a catalyst produced dehydrogenation because it exerts a greater (or less) force than does one that produces dehydration. It seems to me more reasonable to believe that there are differences in kind rather than of degree of dislocation of the molecule. Instead of there being four or five kinds of catalyst-ethanol compounds or four or five degrees of unsaturation of catalyst atoms, the various reactions are dependent upon the relationship in space of the catalyst atoms which are *simultaneously* exerting their attractive forces upon the organic molecule, thereby distorting it in different ways. It seems probable that differences in the degree of unsaturation of catalyst atoms as well as the geometrical relationship of these active points are important factors in catalytic reactions.

---

[1] Proc. Roy. Soc., **98A**, 13 (1920).

[2] A. C. S. Spring Meeting, Baltimore (1925).

[3] Chimie et Ind., **12**, No. 2 (1924); Deuxième Conseil, Institut Solvay (1925)

"Emphasis should be placed on the fact that there are two distinct phases to these catalytic reactions, and that these two phases apparently have no relationship to each other. The one phase has to do with *how much* material reacts under a given set of conditions and the other phase has to do with the ratio of the reactions that take place. The first phase may very well have an intimate relationship to the adsorptive capacity of the catalyst. It varies with very slight changes in the method of preparation of the catalyst. In general this behavior of the catalyst is not readily duplicated with different preparations from the same materials. In marked contrast to this is the case of duplication of the characteristics of the second phase; provided the catalyst is made by the same method, i.e. by ignition of a carbonate, dehydration of a hydroxide, hydrolysis of an alkoxide, etc. Two catalysts made from a butoxide may differ from each other by as much as a 100% in the *amount* of material that they will cause to react in unit time, but the proportion of the reactions induced will differ by only a per cent or so. The one characteristic of the catalyst is dependent, I believe, upon the number of active adsorbing centers, the other upon the characteristics of the surface at those active points. The distinctness of these two characteristics of catalysts has never been sufficiently realized.

"The titanias from the "oxytitanate" and from the sodium titanate were not duplicatable for a very simple reason. The "oxytitanate" was a mixture and the hydrolysis of sodium titanate gives a mixture of products. It is not surprising that the catalysts derived from different mixtures were not identical. If "alkaline or salt poisons" caused the differences in catalytic activity, what caused the differences between those catalysts that had been prepared by the hydrolysis of products that had been repeatedly distilled? The explanation given would only account for differences in the behavior of two catalysts out of twenty or more and seems of little importance when it is known that these catalysts were derived from impure mixtures."

General Conclusions

This report has attempted to demonstrate that, in so far as the contact agent itself is concerned, the experimental researches of the past five years have supplied a consistent, intelligible picture of its nature and of its special properties. This picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto. For, it shows that the properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed; that it is rather the properties of the individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change. The ordinary general, inorganic, and organic chemistry of substances is concerned with the reactions and properties of many million millions of examples of such atoms or molecules, and the result given is a statistical average covering all the cases. The properties of the contact agent, especially in catalytic reactions difficultly achieved, are those of the aristocracy of the atomic or molecular species concerned, and are as different from the statistical average behavior of the crowd as the actions of an educated minority of people should be different from that of an indiscriminately collected mob.

That conclusion reached, however, oceans of uncharted knowledge open beyond. We seem to be forced to the conclusion that we know little or nothing concerning the effect which such aristocracies of atoms exercise on the impinging reactants. Our knowledge is almost negligible on the nature of the activation process induced in the reactant by its association with the catalyst. And it would seem that, before the whole problem can be solved, this must be learned. We return here to a sentence from the First Report, "the general problem of activation is of such fundamental importance that every chemist in the world, should be keeping it in mind so as to be ready to do his share in the solution." One would add to that the hope that he will not only keep it in mind but in hand as well, so that by experimental test the problem may achieve solution. The technique of the physicist in his study of sub-atomic phenomena is needed. The technique of the photochemist must be employed as an aid. Yet more and more experimental work, wisely conceived and accurately achieved, in the reactivity of molecules on contact catalysts is also indispensable.

THE SORPTION OF VAPORS BY ALUMINA

BY L. A. MUNRO AND F. M. G. JOHNSON

WATER

It has long been known that alumina would catalyse dehydration reactions, and this property of alumina has been extensively investigated by Sabatier[1]. Adsorption and catalysis may appear to be related phenomena, and several investigators have made a study of the sorptive power of different catalysts[2]. The sorptive power of alumina has, however, received very little attention[3]. It has been noted in the first part of this investigation[4] that alumina took up a greater amount of water than of any other vapor. This fact, in addition to the knowledge that alumina is such a good catalyst for dehydration of alcohols, etc., suggested that an accurate study of the sorption of water would be of interest. This research was undertaken with this object in view.

Method

A dynamic method, such as that previously used[4], while of sufficient accuracy for a study of a general nature, is not suited for the measurement of sorption over a temperature range, nor can it be used when it is desired to obtain any great accuracy. In order that the study might still be pursued by a dynamic method it was necessary to design an apparatus which would give accurate measurements at different temperatures and concentrations. Such an apparatus has been constructed.

A known volume of air (measured directly by a specially designed gas meter), is saturated with vapor at a definite temperature, and the resulting mixture is passed through the sorption tube at a higher fixed temperature. The course of sorption is followed by weighing the sorbent at intervals. With this apparatus the weighing of the alumina is done without removing it from the bath and consequently at bath temperature. The great advantage of this is in the time saved. The amount of vapor supplied is calculated from the volume of air saturated, and the vapor pressure of the saturating liquid.

Apparatus

The entire apparatus was constructed of glass with fused joints. In Fig. 1 are shown the Maass control[5] and counting device, which are mounted on a wooden stand. By means of the control M, attached to a water pump, alternate suction and pressure are applied to the miniature Töpler pump C,

---

[1] "Catalysis in Organic Chemistry."

[2] Guichard: Bull., **31**, 647 (1922); Benton: J. Am. Chem. Soc., **45**, 887, 901 (1923); Beebe and Taylor: **46**, 43 (1924).

[3] Denver: Proc. Roy. Inst., **18**, 435 (1906); Munro and Johnson: Ind. Eng. Chem., **17**, 88 (1925); Pearce and Alvarado: J. Phys. Chem., **29**, 256 (1925).

[4] Munro and Johnson: Ind. Eng. Chem., **29**, 256 (1925).

[5] J. Am. Chem. Soc., **41**, 35 (1919).

(Fig. 2.) T, is a tap which serves to regulate the flow of mercury back into M, and thus adjusts the time interval between consecutive strokes of the pump C. The counter, operated by the piston P, counts the number of times the suction is released by M and thus the number of strokes of the pump. In order to prevent the mercury column in the U tube from hitting the piston P with too much momentum when the suction is broken, a large plug of glass wool is inserted at X. This greatly reduces the velocity of the fall.

The other parts of the glass apparatus are shown in Fig. 2. No. 1 and 2 are thermostats, no. 1 being at a temperature greater than no. 2. These are joined by a tube at M. The baths and the connecting tubes were heavily lagged with asbestos paper. When suction is applied, the mercury in C is drawn into the bulb B, filling it. Air, free from CO_2 and water, enters C through A, at atmospheric pressure. As the suction continues, a small volume of mercury rises in the capillary tube, reaching the level x′, at which time the suction is broken by the control M, (Fig. 1), and atmospheric pressure restored. The mercury flows back into C, cutting off the air at the same point each time and rising to the fixed level in the very fine capillary D.

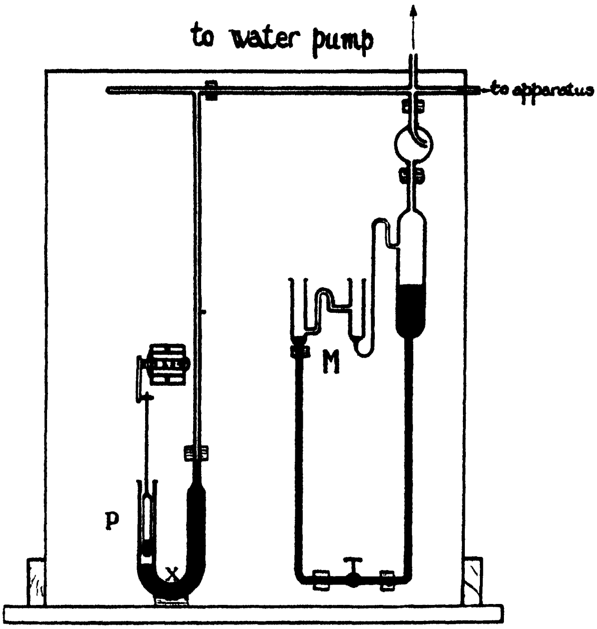


FIG. 1

The air then passes through the mercury valve E. It enters a piece of apparatus designed to make the flow of air continuous, and at the same time to have it under uniform pressure. This is accomplished in the following way: A capillary of sufficient fineness to give the desired rate of flow of the entering air, is inserted at J. The air from E has two routes available at F; through J at the definite rate, or through the tube F. The large amount enters the vessel G through the latter tube. G acts as a gas reservoir and can move upward and downward in the chamber I. The entering air forces G upward against the pressure due to the head of mercury in H. The rising tube is guided at the top and the bottom as shown in the diagram. Mercury fills I to the level X making a seal between F and G. As soon as the air ceases to enter E the reservoir G begins to descend, due to the weight of mercury in H, the air escaping through J. Since G is made from very thin glass the difference in pressure due to the difference in volume of the glass immersed in the mercury at any time is negligible compared to the pressure caused by H. By adjusting the mercury in H, the rate of flow of air through J may be regulated.

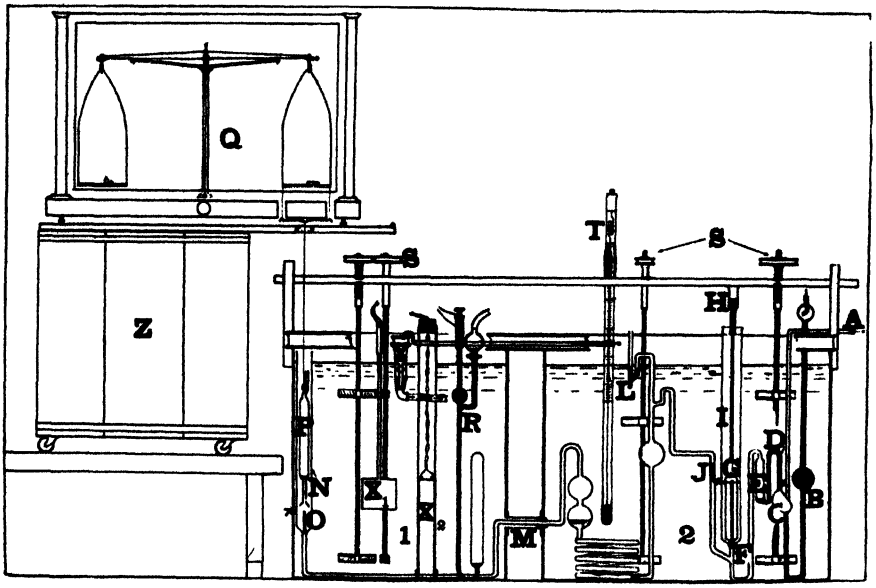


FIG. 2

The air next passes to a wide glass spiral containing glass beads and filled with the saturating liquid. Bubbles are formed at the bottom of the spiral. These travel a considerable distance (90 cm) in contact with the liquid and become saturated. The mixture passes along to M where it enters a region of higher fixed temperature, in bath 1.

Beyond M the mixture goes to the sorption apparatus N. P, the tube containing the alumina is provided with a narrow tube at each end. The upper tube is bent and a little glass hook is affixed to the side, so that the tube may be suspended vertically in the tube N. The lower tube is of just sufficient width to admit the tube O and has a flanged end which serves as a guide for the tube O when P is being lowered. A closed connection is made between O and P by means of a mercury seal. The tube P can be raised and suspended to one arm of the balance Q, by means of a silver wire. Q is mounted on a moveable stand Z, so that on the completion of a weighing, P can be detached from the balance wire and then lowered over O by another wire when the balance is moved out of the way. R is a thermo-regulator. The stirrers are denoted by S. T is a Beckmann thermometer. X_1 and X_2 are heaters. Y is a constant level arrangement for bath 1.

The saturator can be refilled by means of the device L. The mercury in L is removed by a pipette and the saturating liquid is poured into the long arm, siphoning over into the saturator. This filling can be done without getting any air into the apparatus, because the short branch of L can be kept full of liquid since it is above the surface of the warm bath. Hence the mercury level is brought just below the branch tube, the short tube is still sealed by liquid which siphons over when more liquid is added. The mercury is replaced and the short arm remains filled with liquid. The thermo-regulator and heating units for thermostat no. 2 and the thermometer for no. 1 are not shown in the diagram.

Possible Sources of Error in the Apparatus

It is necessary to make a critical survey of the apparatus in order to get a reliable estimate of the accuracy obtainable.

The first thing to be considered is the volume of air delivered by C. The same amount of air must enter and the same amount must be discharged each time. The factors which will affect this will be the pressure of the entering air and the relative position of the mercury in C at the beginning and end of each up stroke. The expansion of the mercury in B and C over a temperature range of 30° is not great enough to affect the level to which the mercury falls in C. If initially the level to which the mercury fell was just below the air inlet and subsequent lowering of temperature caused the level to sink well down in the tube leading to B, some error might be introduced. Under experimental conditions however, this never happens. Differences in temperature will make very little difference in the height to which the mercury will rise in the capillary D, because the diameter of the bulb E is so large that an expansion of 10 per cent would only cause a slight change in level. The capillary D is of a very fine bore so that any such change in level would have practically no effect on the volume of air delivered.

The volume of air entering E is also independent of the pressure in other parts of the apparatus. The air enters C at atmospheric pressure and shuts off at the same point each time. If the pressure in E did vary, the air in the capillary D would expand or contract, but the effect of as much as one centimetre pressure variation in E would be negligible.

The expansion of the glass over the temperature range used (25-45°) can be neglected.

Calculations of the amount carried over depend on the assumption that the water vapor is of normal density and that Dalton's law is followed by the mixture. That this assumption is justifiable has been shown by Menzies[1]. There is therefore no error inherent in this part of the apparatus.

---

[1] J. Am. Chem. Soc., **42**, 978 (1920).

The amount of vapor which the air will carry over will depend on the temperature of the liquid and the pressure at M. The latter has been reduced to atmospheric pressure by using the sorbent in the form of relatively coarse grains and a loose plug of asbestos to retain the alumina.

The other place in the apparatus which may introduce experimental error is the arrangement for weighing the sorbent. On raising P from the mercury, a volume of air equal to the volume of the inlet tube O will be drawn into the upper part of P. In order that this air might not come in contact with the alumina and change the concentration of the equilibrium mixture, the tube was never completely filled with alumina. This entering air would therefore have no effect and would be expelled by the exit gases, if not by the replacement of the tube over O.

In order that the guiding flange of P might not entrap air when lowered into the mercury, with a resulting dilution of the entering gas, a small hole was blown in the wall of the tube just above the flange. This allowed the air to escape. Hence error caused by the dilution of the vapor has been eliminated.

The Temperature Control

The temperatures are controlled by thermostats. Bath no. 2 in which the apparatus A to M is placed, is heated electrically. Temperature variation in this bath was shown by a Beckmann thermometer to be $<.02$°C. The temperatures of the baths were set by a standard thermometer.

Thermostat 1 was heated by X_1 and X_2, and the temperature kept constant by varying the resistance in the X_1 circuit by means of a relay in series with the thermo-regulator R. At 80° the temperature variation was less than 0.1°, while at lower temperatures it was less than 0.05°.

When N was open to the air, as in the case when a weighing is being made, the temperature in N at a point 2.5 cm below the surface of the bath was found to be 0.5° below the temperature of the bath (80°). Five cm. below the surface, the temperature was 80°. This means that even during weighings, the alumina was kept at constant temperature.

The chief source of error is the weighing of the tube P. The tube can be weighed to within ± .0002 g. This may amount to as much as a few percent of the increase in weight between consecutive weighings, but seldom introduces an error of more than .1% in the saturation value.

The amount of vapor supplied by one stroke of the pump is given by the product:

$$\frac{273 \,.\, p \,.\, V \,.\, M.}{T. \,(760\text{-}p)\, .22400} \text{ grams.}$$

Where p is the vapor pressure of the liquid,
V, the volume of air supplied,
M, the molecular weight of the vapor,
T, the absolute temperature.

p is the factor involving the greatest error, which may in some cases be as high as 0.5%. Any back pressure caused by the alumina in P will introduce some error, but the total error in this product is not greater than 1%.

The preparation of the alumina, its subsequent treatment and its age, all affect its sorptive power. When the gels are prepared in the same manner accurate results can be obtained, and these results can be reproduced.

Calibration

The pump C was calibrated by measuring the volume of air at constant temperature delivered by a known number of strokes of the pump. Three consecutive determinations gave the values 13.18, 13.17, 13.18 c. c. as the volume of air delivered per stroke. This was checked a month later and the value 13.18 c.c. obtained.

Preparation of the Alumina

At first the alumina was prepared from the hydroxide obtained from the Mallinckrodt Chemical Co. This was found to be too fine for use in this type of apparatus as it caused considerable back pressure. The alumina used in this work was prepared by precipitating the hydroxide from a hot solution of 300 g. of the nitrate in two litres of water, by concentrated ammonium hydroxide. It was then diluted to 6 litres and boiled until there was no odor of ammonia. After settling the gel was washed with distilled water until free from nitrates as shown by the phenol sulphonic acid test. Any traces of ammonium nitrate remaining would be decomposed at the temperature used for dehydration. The gel was then dried for twenty-four hours at 100° after which a known weight of the gel (10-16 mesh) was placed in a sorption tube and heated in an air bath for one hour at 300°. The total water content was determined by blasting a separate sample of gel for several hours. The state of hydration is determined from the loss in weight of the alumina tube.

Composition of the Gel

Kuhn[1] distinguishes between "water capacity" and "water intensity" of gels. The intensity is determined by the strength of the attraction between the water molecules and the molecules or particles of gel. It is probable that water intensity of alumina is much greater than that of silica gel since the latter forms no definite hydrates whereas several hydrates of alumina occur in nature. Martin[2] and von Bemmelen[3] have shown that the true hydroxide is obtained when an aluminate is decomposed by HCl. Milligan[4] has found that the true hydroxide is stable up to 145°. Hagewaka[5] has shown that the water of crystallization changes to sorbed water at 200° and Fricke and Wever[6], on the other hand, have found that alumina gel slowly changes to the crystalline hydrargillite, and if heated at 100° for some time, shows a tendency to revert to microcrystalline bauxite.

---

[1] Kolloid-Z., **35**, 276 (1924).
[2] Mon. Sci., **5**, 225 (1915).
[3] Rec. Trav. chim., **7**, 75 (1888).
[4] J. Phys. Chem., **26**, 247 (1922).
[5] Kolloid-Z., **32**, 1154.
[6] Z. anorg. Chem., **135**, 321 (1924).

The question as to the composition of alumina gel has received the attention of a number of investigators and the opinion of most of these has been that the gel is not $Al(OH)_3$. Willstätter[1] has recently published a series of papers on alumina gel, in one of which he describes the drying curves for gels prepared by different methods. In almost every case the water content of the sample remained constant as the temperature was raised to 120°. These different gels had dissimilar properties, which he attributed to the presence of a different number of alumina-water complexes in each. He supposed that the $Al(OH)_3$ is the primal hydrate which loses water, leaving partially dehydrated molecules. These being possessed of strong residual fields unite to form molecular groups with varying amounts of water. These groups may be represented by the general formula $Al_n(OH)_{3n}.xH_2O$. It is therefore probable that when water comes in contact with this molecular complex it will be attracted by forces that are distinctly chemical.

It is impossible however to imagine that all the water in the gel is held by residual valences; some must certainly be held by capillary condensation, beyond the range of the unsaturated forces of the alumina complexes. Foote and Richards[2] consider that the gel contains both "chemically combined" and sorbed water. By the term "chemically combined" they doubtless mean that the water is held by what Langmuir calls "primary valence". Since the difference between the forces that bring about chemical combination and those that cause adsorption is a quantitative rather than a qualitative one, it is sufficient to state that the water in alumina gel is bound by chemical forces and by condensation in the capillaries. Experimental results previously described[3] show that alumina takes up a greater amount of water than of any other vapor. This fact supports the theory of selective adsorption. The results to be described in this paper show that capillary condensation also plays an important part in the sorption of water vapor by alumina.

Results

It has been found that better agreement between the results for different samples of alumina is obtained when the results are expressed as mg. per gram of *active* Al_2O_3 instead of *sorbent* ($Al_2O_3 . xH_2O$). The amount of active Al_2O_3 is readily calculated from the dehydration when the original water content of the gel is known[4]. The results of this investigation are expressed in this manner.

Sample Calculation

Two typical examples of the results obtainable with this apparatus are given in detail (Tables I and II) in order to show the method of calculation and the agreement between the calculated and observed values of the amount of vapor supplied.

---

[1] Ber., **57**, 58 (1924).

[2] J. Am. Chem. Soc., **38**, 588 (1916).

[3] Munro and Johnson: Ind. Eng. Chem., **17**, 88 (1925).

[4] Munro and Johnson: Ind. Eng. Chem., **17**, 88 (1925).

TABLE I

Tube 3. Weight of tube 16.0460 g. Gel. .2.469 g. Active Al_2O_3, 1.464 g.
Bath no. 1 at 80.0°C. Bath no. 2 at 45.00° ± .02
Rate 1 stroke / min.
Vapor pressure 72 mm
Amount of vapor supplied per 100 strokes of pump =

$$\frac{18\times72\times13.18\times273}{224\times689\times318} = .0941\text{ g}$$

Total strokes	Weight supplied	Amt. supplied in mg/g Al_2O_3	Gain in wt. of alumina	Amt. sorbed in mg/g Al_2O_3	Hours
65	0.0612	41.7	0.0610	41.7	1.1
110	. 0.1035*	70.7	0.1030	70.7	1.8
200	0.1882	128.5	0.1562	106.7	3.3
370	0.3418	238.0	0.1675	114.4	6.2
460	0.4330	296.0	0.1765	120.5	7.7
770	0.7246	495.0	0.1806	123.4	12.8
1370	1.2900	880.0	0.1850	126 0	22.8
1752	1.6480	1126.0	0.1864	127.0	29.2
2060	1.938	1324.0	0.1872	128.0	34.3
2360	2.921	1517.0	0.1900	130.0	39.3

*Sorption is probably complete, since difference between calculated and observed values, is less than 0.5%.

TABLE II

Tube 5* Weight of tube 15.1452 g. Gel. 1.810 g. Active Al_2O_3, 1.054 g.
Alumina (Bath no. 1) at 40.0° Saturator (Bath no. 2) at 30.0°
Rate 1 stroke per minute
Partial pressure 31.8 mm.
Amount of vapor supplied per 100 strokes of pump =

$$\frac{18\times31.8\times13.18\times273}{224\times730\times303} = .0416\text{ g.}$$

*(Resistance to air flow, 1.5 mm)

65	0.0269	25.6	0.0268	25.6	1.11
175	0.0728	69.0	0.0730	69.2	2.9
280	0.1165	110.5	0.1162	110.4	4.7
380	0.1580	150.0	0.1400	133.	6.3
500	0.2080	197.0	0.1534	147.	8.3
630	0.2630	249.0	0.1640	156.	10.5
862	0.3585	340.0	0.1720	163.	14.4
1142	0.4750	451.0	0.1768	168.	19.0
1397	0.5812	551.0	0.1800	171.	23.3
1435	0.5968	566.0	0.1832	174.	23.9
2207	0.9180	871.0	0.1864	177.	36.8
2590	1.077—	1022.0	0.1866	177.	43.2

TABLE III

Alumina at 80° Partial pressure 72.7 mm.

Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
40.1	40.1	1.0
64.3	61.0	1.67
109.2	71.1	2.83
161.	73.7	4.16
642.	78.4	16.7

TABLE IIIa

Alumina at 80° Partial pressure 72.7 mm.

Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
32.1	32.1	.83
64.2	60.9	1.67
141.3	72.9	5.60
212.	75.3	5.50
578.	77.8	15.0
994.	82.1	25.8

TABLE IV

Alumina at 80° Partial pressure 55 mm.

24.3	23.4	.85
50.9	51.0	1.75
97.0	65.2	3.33
170.	68.0	5.83
509.	71.4	17.5
580.	71.4	20.0

TABLE V

Alumina at 80° Partial pressure 42.2 mm.

19.1	20.5	.66
43.9	43.7	1.55
134.	57.4	4.67
430.	61.6	15.0
28.	28.0	1.33
111.	58.0	5.33
151.	59.3	7.25
471.	62.9	22.6

TABLE VI

Alumina at 80° Partial pressure 31.8 mm.

54.2	45.6	2.3
79.8	49.9	3.3
459.	54.4	19.1
558.	55.8	23.3
660.	53.9	27.6

VII

Alumina at 60° Partial pressure 55 mm.

29.4	29.6	1.0
62.8	62.5	2.2
353.	114.5	12.2
546.	115.7	18.8
677.	115.7	23.4

TABLE VIII

Alumina at 60° Partial pressure 42.2 mm.

24.3	24.7	.83
76.8	73.9	2.63
120.	87.9	4.16
170.	94.4	5.90
259.	97.4	9.00
341.	98.9	11.2
715.	110.	24.8

TABLE IX

Alumina at 60° Partial pressure 31.8 mm.

61.2	62.6	2.58
90.6	77.0	3.83
122.4	80.8	5.17
428.	89.2	18.1
580.	89.2	24.5

TABLE X

Alumina at 50° Partial pressure 72.7 mm.

Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
64.4	63.0	1.4
96.7	94.7	2.5
226.	195.	4.2
907.	294.	16.8
1360.	316.	25.1
1720.	330.	31.8
2626.	346.	48.2
2980.	349.	55.0
3190.	352.	58.9
4645.	376.	83.9
4745.	378.	87.6
5428.	379.	100.3
5595.	383.	103.3

TABLE XI

Alumina at 50° Partial pressure 55 mm.

Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
69.7	69.9	1.32
199.	142.2	3.78
247.	149.0	4.7
343.	158.6	6.5
455.	165.	8.6
1054.	170.	20.0
1260.	172.	23.9

TABLE XII

Alumina at 50° Partial pressure 42.2 mm.

34.5	34.5	.87
61.1	61.1	1.53
130.2	117.9	3.27
193.9	128.8	4.87
305.5	135.1	7.68
390.	138.	9.80
465.	139.	11.7
558.	139.4	14.0
1127.	141.	28.3

TABLE XIII

Alumina at 50° Partial pressure 31.8 mm.

19.7	19.7	.61
42.6	42.7	1.26
61.8	61.6	2.00
100.3	91.0	3.25
116.	97.2	3.75
143.	105.3	4.63
175.	107.4	5.65
270.	112.0	8.75
642.	117.	20.8

TABLE XIV

Alumina at 50.1°	Partial pressure 23.5 mm.	
26.6	26.6	1.15
89.8	82.5	3.88
169.	92.8	7.38
380.	97.	16.5
480.	101.9	20.9
647.	102.	28.1

TABLE XV

Alumina at 40°	Partial pressure	at 40
32.0	32.0	0.2
105.6	105.6	3.8
167.	169.	5.9
486.	330.	17.0
643.	382.	22.5
690.	396.	24.2
790.	424.	27.7
862.	450.	30.2
1195.	526.	41.8
1282.	547.	45.0
1348.	561.	47.2
1500.	593.	52.5
1640.	620.	57.3
1990.	678.	69.5
2070.	691.	72.5
2220.	719.	77.6
2310.	738.	81.0
2720.	752.	110.

TABLE XVI

Alumina at 40°	Partial pressure 52.5 mm.	
Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
49.3	49.3	1.05
94.2	94.2	2.01
197.4	182.4	4.22
253.3	209.	5.42
311.8	232.	6.67
357.	249.	7.64
598.	315.	12.8
669.	335.	14.3
1260.	432.	27.0
1345.	435.	28.7
1449.	451.	31.0
1825.	502.	39.0
2468.	559.	52.8
2877.	608.	61.5
3137.	628.	67.1
3774.	675.	80.7
4300.	717.	92.0
4613.	764.	98.6
4937.	782.	105.2
5392.	802.	115.3

TABLE XVII

Alumina at 40°	Partial pressure 49.7 mm.	
Amt. of vapor supplied, in mg./g. Al_2O_3	Amt. of vapor sorbed, in mg./g. Al_2O_3	Time in hours
47.3	47.3	1.3
120.	120.	3.2
190.	175.	4.2
238.	196.	5.2
310.	220.	6.5
324	243.	7.0
376.	258.	8.2
417.	265.	9.1
1043.	350.	22.6
1139.	364.	24.7
1297.	376.	27.4
1381.	387.	29.9
2220.	473.	48.1
2430.	484.	52.4
2540.	498.	55.3
2750.	513.	59.8
2870.	520.	62.4
3390.	549.	73.5
3650.	565.	79.3

TABLE XVIII

Alumina at 40°	Partial pressure 43.3 mm.	
48.3	48.3	3.3
129.	115.8	8.9
275.	177.3	19.0
301.	184.4	20.8
348.	196.5	24.0
411.	213.	28.4
452.	220.	31.2
611.	234.	42.2
712.	242.	49.1
811.	249.	56.0
927.	257.	64.
1019.	258.	72.
1086.	259.	75.
1276.	266.	88.
1390.	270.	96.
1469.	272.	101.

TABLE XIX

Alumina at 40°	Partial pressure 23.5 mm.	
28.3	28.3	1.67
48.1	45.5	2.83
166.	109.1	7.5
159.	116.6	9.3
229.	126.7	13.5
275.	129.7	16.2
331.	131.8	19.5
399.	132.0	23.1
589.	134.	34.6
	134.	44.7

TABLE XX

Alumina at 35.5°	Partial pressure 31.8 mm.
Amt. sorbed in mg./g.	Amt. supplied in mg./g.
111.5	113.1
115.2	155.7
158.	183.
185.	263.
211.	386.
236.	715.
251.	1097.
264.	1520.
266.	1782.
267.	2372.

In Tables III-XIX are given the results for alumina at 80, 60, 50 and 40° and for partial pressures of from 72.7 to 23.5 mm. The curves for 40° (Tables XV-XIX) are given in Fig. 3. These are typical, and the curves for the other temperatures are therefore omitted in order to save space. The broken line in Fig. 3 is the total sorption line, which the curve follows when the alumina is 100% efficient.

The sorption was first measured when the alumina and saturator were both at 40° i.e. $p/P = 1$. Other experiments (Tables XVI and XVII) were carried out in order to find how the sorption varied with small changes in concentration of vapor near the saturation pressure. The results are shown graphically in curves 1, 2 and 3, Fig. 3. In the experiments with water at a partial pressure of 52.5 mm and 55 mm it was observed that the gel became transparent before the last few points shown on the curves (1 and 2) were reached. Owing to the proximity of the temperature of the alumina and the saturator, condensation of the vapor is brought about by very slight changes in temperature and it is therefore very difficult to determine the true saturation value.

Curves 4, 5 and 6 are for partial pressures of 42.2, 31.8, and 23.5 mm. respectively. In one experiment the alumina was kept at 35.5°, the partial pressure of the vapor being 31.8 mm. The curve is shown in Fig. 3 (No. 7) in order that the results may be compared with those obtained when the alumina was at 40°.

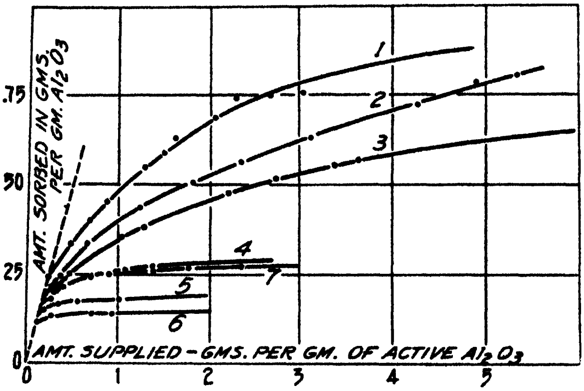


FIG. 3

The Sorption Isotherm

The saturation value represents the amount of vapor held by the sorbent when in equilibrium with a certain partial pressure of water vapor. By plotting these values against the partial pressure, typical isotherms are obtained. In Fig. 4 are given the isotherms for 80, 60, 50, and 40°. The curves for 80 and 60° as well as the lower part of the 50° isotherm resemble the curves obtained by other investigators for the sorption of gases on charcoal and silica gel by static methods. Freundlich's equation was therefore applied to these curves and it has been found that when the log of the saturation value is plotted against the log of the partial pressure straight lines are obtained. (Curves 1 and 2, Fig. 5).

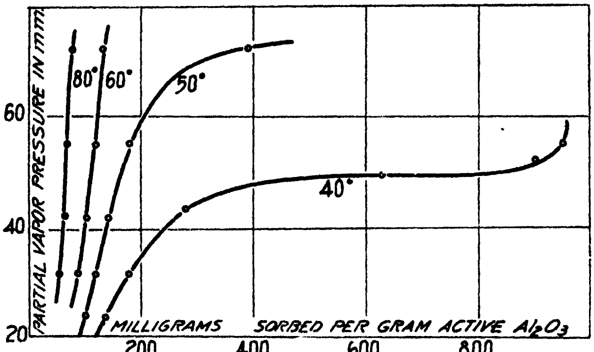
Patrick[1] related the volume of *liquid* sorbed to the relative partial pressure of the vapor and the surface tension of the liquid at the temperature of the sorbent. His equation, which is a modification of the Freundlich equation involving new constants, reads; $V = K\ (Sp/P)^{1/n}$ where p is the partial pressure of vapor, P is the vapor pressure of liquid at the temperature of the sorbent, S is the surface tension of liquid at the temperature of the sorbent, and K and n are constants. His equation also demands a straight line when log V is plotted against log Sp/P.

---

[1] J. Am. Chem. Soc., **38**, 588 (1916).

The different values of these factors are given below:

Temperature.	Sp/P					V.				
80°	5.58	7.41	9.65	12.64		55.6	64.4	73.9	84.5	
60°	14.1	18.6	24.3	31.8		90.2	105.1	120.	132.	
50°	17.2	23.3	30.9	40.3	52.8	103.	118.	143.	174.	386.



ISOTHERMS FOR WATER. ALUMINA AT 40°, 50°, 60°, & 80°

FIG. 4

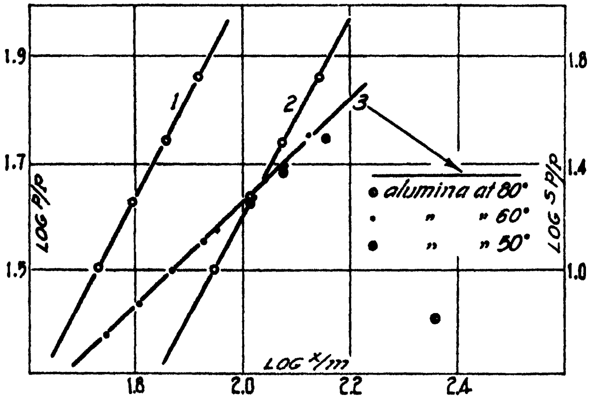


FIG. 5

The curve constructed from the logs of these is given in Fig. 5 (curve 3). Patrick's equation therefore applies to the 80° and 60° isotherm.

It will be noted that the 40° curve, Fig. 4 changes direction and flattens as the partial pressure of the vapor approaches the vapor pressure of the liquid at the temperature of the alumina. This undoubtedly represents the filling of the minute capillaries of the alumina with water. Neither Freundlich's nor Patrick's equation applies to this curve.

Trouton's equation which Anderson[1] used to calculate the radius of the capillaries in silica gel cannot rightly be applied to the curve for 40°, since in this case the curve represents the filling of the capillaries, and as Anderson and others have shown, when air is present the capillaries fill at a higher partial pressure than that at which they are emptied. The radius as demined by applying Trouton's equation to this curve will therefore be much smaller than the true radius.

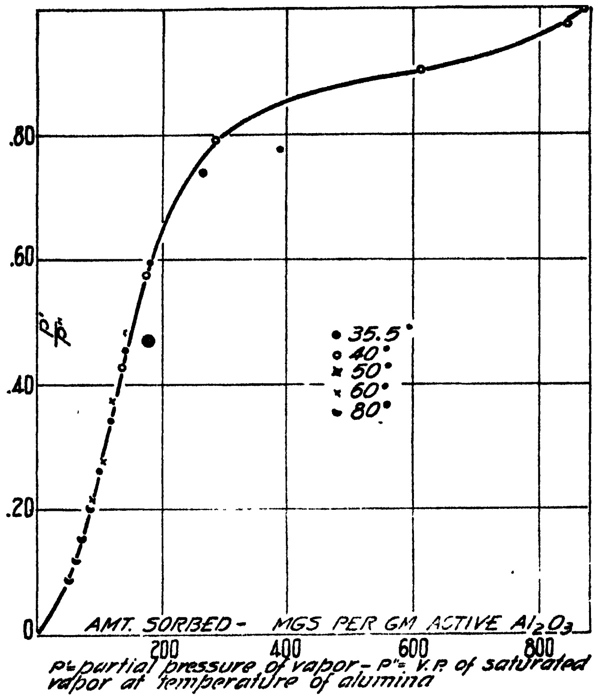


FIG. 6

Trouton's Sorption Rule

Trouton[2] considered that the amount of vapor taken up is independent of the temperature but dependent solely on the ratio of the partial pressure of the vapor to the saturation pressure of the vapor at the temperature of the sorbent. The saturation values have been plotted against the ratio p/P in Fig. 6. It will be seen that all the points fall on approximately the same curve. Trouton's rule may therefore be considered to hold approximately.

Relative Sorption Velocity

In Fig. 7 are shown the relative rates of sorption of water by alumina at 50° for different concentrations. These curves are similar in appearance to those obtained by Harned[1] for the adsorption of gases by charcoal, but of course a quantitative comparison cannot be made since the velocity of flow and the dimensions of the tubes were not the same. In these experiments the rate of flow was 13 cc/min. and the cross section of the tube .39 sq. cm. Similar velocity curves can also be constructed for the other temperatures.

---

[1] Z. physik. Chem., 88, 191 (1914).

[2] Proc. Roy. Soc., 77, 292 (1906).

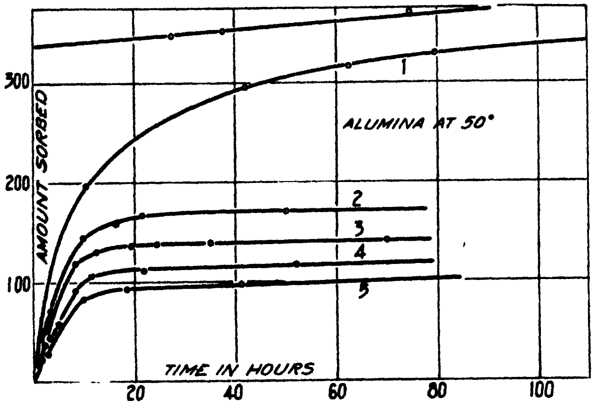


FIG. 7

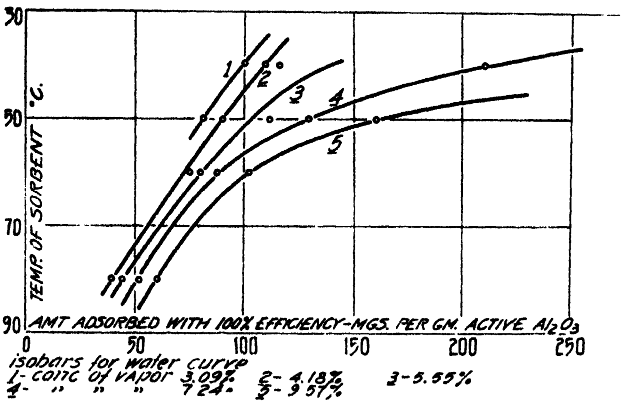


FIG. 8

Efficiency of the Alumina

A knowledge of the efficiency of a sorbent under different conditions is of very great importance in any technical process. This is particularly true of gas mask sorbents where the efficiency must be high enough to reduce the concentration of gas to below .0001% in a very short period of time. In other applications of the sorptive power of solids the demands are not so rigorous, but the efficiency of the sorbent is still of importance. Any technical process using alumina as a drying agent would require information on the variation of the efficiency of the alumina with time, temperature and concentration. The efficiency of other vapors will depend on the relative sorption velocities under the same conditions.

---

[1] J. Am. Chem. Soc., 42, 920 (1920).

The way in which temperature affects the amount which the alumina will take up before the break point is reached, given by the amount of water sorbed with 100% efficiency, is shown in Fig. 8. In this figure curve

1. represents a concentration of 3.09%
2. " " " " 4.18%
3. " " " " 5.55%
4. " " " " 7.24%
5. " " " " 9.57%

water in the entering air-vapor mixture.

In many cases information as to the efficiency of the sorbent during the whole sorption process is of interest. There are several ways in which such information may be obtained. Bohart and Adams[1] give transmission curves which show the percent of entering vapor which is unsorbed or transmitted at any time, and give equations to fit their curves. The same information is given by the curves for water (Fig. 3) since the amount transmitted or unsorbed is given by the distance between the curve and the total sorption line. Efficiency-time curves can be constructed from the data given in the tables.

Summary

1. The sorption of water vapor has been measured at different temperatures and concentrations.
2. Both Freundlich's and Patrick's equations apply to the isotherms for 80 and 80°C. Neither applies to those isotherms obtained when the partial pressures approach the vapor pressure of the liquid at the temperature of the sorbent.
3. Trouton's rule holds approximately.
4. Curves are given showing the change in efficiency with temperature and concentration.
5. Sorption-time curves of the ordinary type are obtained.

Acknowledgment

This research was carried out under tenure of a studentship from the Research Council of Canada, which is hereby gratefully acknowledged.

Department of Chemistry,
McGill University,
Montreal.

---

[1] J. Am. Chem. Soc., **42**, 523 (1920).

EQUILIBRIUM IN COLLOID SYSTEMS

BY OSCAR KNEFLER RICE

Some years ago Tolman[1] wrote two articles in which he developed a generalized phase rule, and applied it to divided and dispersed systems. He considered systems in which a phase might be divided into several regions—for example, two pieces of ice form two regions but only one phase. He developed a special phase rule for the cases where some of the regions were identical; and he found that in any one-component system two regions must either be identical or have at least two variables differ in value, while in a two-component system two regions must be identical or have at least three variables different. In the ordinary two-component colloid systems a colloid particle, which is a region, can change in two independent variables only—size, say, and concentration of one component. (Tolman assumes, and I shall always, that the particles are spherical.) Hence for equilibrium all the particles must be identical. In the case of electrically charged particles, however, another possibly independent variable is introduced. It is the purpose of the present article to develop a generalized phase rule in a form in which it possesses the practical advantage of giving the proper number of degrees of freedom without the previous consideration of identical phases, and then to apply it to the case of electrically charged colloids, showing that the possibility of various electrical conditions does not introduce extra degrees of freedom. It is also desired to consider the dynamics of the above cases, with especial regard to the criterion of stability, which I believe to be different from the one Tolman has given.

The Phase Rule

The number of variables we choose to consider in the development of our phase rule is a somewhat arbitrary matter; but we must choose them to completely determine the system. Inclusion of extra unnecessary variables leads to an equal number of extra equations, and so makes no difference in the phase rule. In a system of c components and r regions we will take the following as variables:

1. The c concentrations in each of the r regions, cr in all.

2. The c fugacities in each of the r regions, cr in all.

3. The temperature, which is assumed to be the same throughout all the regions.

4. The n other variables in each of the regions (including the pressure which is not assumed necessarily to be the same throughout) which serve to specify the state of the regions, nr in all.

5. Any other variables, v in number, which cannot be associated with any particular regions or which affect only a few regions.

---

[1] Tolman: J. Am. Chem. Soc., 35, 307-333 (1913).

At times we may neglect certain variables, which have very little effect on the problem at hand. This is continually done in phase rule work, and its permissibility for purposes of approximation is discussed in Tolman's articles[1].

We have, then $2cr + nr + 1 + v$ variables.

There are the following equations:

1. One equation for each region, stating that the sum of all the concentrations, expressed in per cent, gives 100 per cent; *r* in all.

2. $r - 1$ equations for each component, stating that the fugacity in each region is the same; $(r - 1)c$ in all.

3. *r* equations for each component stating that the fugacity is a function of the other variables, *rc* in all.

4. Any other equations which may exist but which are not included in the above, *e* in all.

The total number of equations is $r + (r - 1)c + rc + e$.

The number of degrees of freedom is, therefore, given by

$$f = 1 - r + c + nr + v - e \qquad (1)$$

We will first attempt to apply this phase rule to colloids which are not electrically charged. We have here two components, one of which chiefly makes up the dispersed phase, the other the dispersing phase, thus making $c = 2$. $n = 1$, for, as we have mentioned above, in this case there is but one independent variable, other than concentration and temperature, for each region; this may be taken as the size of the particle, and for the dispersing phase the pressure. The pressure inside each particle is uniquely determined by the surface tension, the radius, and the external pressure, while the surface tension is determined by the radius of the particle and the other variables. It is seen, then, that either pressure or surface tension might just as well have been taken as the independent variable, and we will use these quantities in many cases interchangeably. We have yet another variable to consider. It is known that the fugacity of the constituents of the dispersing phase and perhaps of the other regions depends on the number of colloid particles per unit volume. Or, instead, we may use as variable the ratio of the total amounts of the two components, which, with the other variables, determines the number of particles per unit volume. So $v = 1$. There are no additional restrictions or relations between the variables, so $e = 0$. Substituting now into (1) $f = 4$. We have completely specified our system if we give temperature, pressure on the dispersing medium, radius of *one* particle, and the ratio of total amounts of the two components. From this we would infer that at equilibrium there is one size of particle, or, at least, only a small number of definite sizes.

We shall now pass to the case where the colloid particles may be charged. Here the fugacities of the various substances concerned will be completely determined if, besides temperature and external pressure, their concentrations, the concentration of electricity, and the surface conditions, electrical and otherwise, are known. It may be necessary to use several variables to specify the conditions at the surface but at equilibrium they will each have a definite value for given concentrations of the components and electricity in the particle and surrounding region, for given geometrical conditions (which we assume are determined by the size of the particle to which the variables relate), and for a given particle density. They are, therefore, not independent, and cannot affect the number of degrees of freedom, under the assumptions made, which would seem to hold very approximately. So $n = 1$, as before. The above discussion naturally intimates that we are going to treat electricity as a component. (Only one kind of electricity is a component, for the electricity is involved in an equilibrium with matter, $A \longrightarrow A^+ +$ an electron, which brings in an equilibrium equation). This necessitates the addition of another equation stating total charge is zero. We now have $c = 3$, $e = 1$, while $v = 1$, as before, so we again have $f = 4$.

---

[1] Tolman: loc. cit.

If the electrical charge is due to ionization the case is not essentially different. One of the ions is then taken as the extra component.

This result may be obtained in another way. Suppose we divide our system into a large number of small regions, within each one of which conditions are approximately uniform[1]. Then conditions in any one region are determined by the temperature, its pressure, its concentrations of substances and electricity, and similar variables for other surrounding regions. The regions are of course battered around in the Brownian movement, but if the particles do not change appreciably when in a state of equilibrium the regions may be considered to maintain their identity, at least for a time, while the effect of surrounding regions, which is doubtless small, is to some extent a statistical mean. If there is a certain definite number of regions each having a definite composition, the ratio of components may no longer be regarded as an independent variable, and if we call $v = 1$ we must add an equation. But the same definiteness in number of regions and their composition fixes the amount of electricity present and eliminates the necessity of another equation stating total charge is zero, so the number of degrees of freedom is the same as before. The rigor of the above treatment may be questioned owing to the Brownian movement and the fact that a region may have a small number of molecules. In fact, all the previous considerations are more or less open to the former objection, as Tolman noted in his treatment of the subject, but the value of results obtained by neglecting Brownian movement will appear later.

The next interesting case is that of a colloid dispersed in a salt solution. Here, counting the electricity as a component we have $c = 4, n = 1, v = 1$ (particle density, say) and $e = 1$ (total charge zero). Hence $f = 5$. So we must fix, say, temperature, outside pressure, relative amounts of colloid substance, solvent, and salt, and the radius of one particle.

From these results it is again to be inferred that a condition of equilibrium is realized when the particles are all of one size, or of a small number of definite sizes. This inference can be readily generalized.

---

[1] See Beattie: J. Am. Chem. Soc., **46**, 2213 (1924).

Stability of the Equilibria

Since in the cases above considered the size of the particles can be fixed at any desired size there will be many such equilibria, but not all of them will be stable. If the equilibrium is unstable its free energy will be a maximum, and any infinitesmal displacement will cause a change in free energy which is zero to the first order of infinitesmals and negative to the second. The condition for stability is that the total free energy of the system shall be a minimum, i.e., that any infinitesmal displacement in the system shall cause a second order increase of free energy. We may have a family of such minima. In this case there may be one or more of these minima which is less than all others immediately adjacent. The stability which exists at any one of the minima in the family we shall designate as temporary stability; if it corresponds to one of the particular minima which is less than its immediate neighbors we shall refer to it as permanent stability; for we would anticipate that a system in which there was thermal agitation would sooner or later revert to stability of the latter type; it must not be forgotten, however, that the words as used here have a special technical meaning. As a matter of fact, in practice we would never expect to see temporary stability, while a system in a permanently stable state would be subject to statistical fluctuations. Experimentally known systems in which the particles all come to a certain stable size[1] are presumably in a permanently stable state in the sense used.

What we shall have to say in the following applies to all colloids which can change continuously in size, and we will reserve the right to use such words as particle and drop, colloid and emulsion, indiscriminately.

There are three distinct kinds of changes possible in ordinary colloid systems: (1) Changes involving transfer of material from the colloid particles into the dispersing medium and *vice versa*, without change in the number of particles (drop-solution changes); (2) changes involving interchange of material between various particles without change in their number (drop-to-drop changes); (3) interchange of material involving change in the number of particles (drop-density. changes).

In order to visualize these phenomena better we will devise a process whereby the changes may be effected. It should be emphasized that these changes take place within a given system, and that whatever steps our hypothetical process may take us through we always have in the initial and final states exactly the same total amount of each component. The machine we will use will merely be a set of reversible cells each of which can transfer one of our components from place to place in our system, or into a standard region to be specified. Thus if we wish to transfer material from one drop to another we have electrodes in each of the drops. If we wish to have a greater number of drops we can have various electrodes in different drops all connected in parallel and connected to an electrode which is in an infinitesmal drop, which we can then build up to the desired size at the expense of the others. This shows that a change from one state to another in which the number of drops is different can never be an infinitesmal displacement in the dynamical sense, for if the drop to be made or removed is of finite size it requires the transference of a finite amount of material. This point should be emphasized, as it carries important consequences. Systems stable with respect to drop-solution and drop-to-drop changes are stable in the way we have called temporary, while if they are also stable with respect to drop-density changes they are permanently stable, as will appear.

---

[1] Tolman: loc. cit.

We will now consider the stability of equilibria in which all the particles have the same size and are similar. One condition for stability is that reversible drop-solution transfers of material shall cause an increment of free energy which is zero to the first order and positive to the second. The same must be, true for free energy changes accompanying reversible drop-to-drop changese with or without change of composition. By examining in detail the case whern there is a drop-to-drop transfer of one component only we can get certain criteria of value.

Let F_i be the free energy[1] of the *i*th drop, referred for convenience to a standard state in which composition and all other variables are the same as in the drop except that there is no pressure due to surface effects, m_{ij} the mass of the *j*th component in it, v_i its volume, and s_i its surface.

Then, in order for the system to be stable $\Sigma_i \delta F_i > 0$ to the second order of small quantities, and $\Sigma_i \delta m_{ij} = 0$, where the summations are to be taken over all the drops. We may then write

$$\Sigma_i \delta F_i = \Sigma_i \frac{\partial F}{\partial m_{ij}} \delta m_{ij} + \tfrac{1}{2} \Sigma_i \frac{\partial^2 F_i}{\partial m_{ij}} (\delta m_{ij})^2$$

to the second order by Maclaurin's expansion. For the case where the particles are alike we may drop the subscripts *i* and write the derivatives outside the summation sign, thus:

$$\Sigma\, \delta F = \frac{\partial F}{\partial m_j} \Sigma \delta m_j + \tfrac{1}{2} \frac{\partial^2 F}{\partial m_j^2} \Sigma\, (\delta m_j)^2 \qquad (2)$$

The first term drops out as $\Sigma \delta m_j = 0$, and since $\Sigma(\delta m_j)^2$ must be positive, for stability $\partial^2 F/\partial m_j^2$ must also be positive. Since under the conditions stated v and s are functions of m_j we may change variables and write

$$\frac{\partial^2 F}{\partial m_j^2} = \frac{\partial}{\partial m_j}\left(\frac{\partial F}{\partial v_j}\frac{\partial v}{\partial m_j}\right) = \frac{\partial^2 F}{\partial v_j^2}\left(\frac{\partial v}{\partial m_j}\right)^2 + \frac{\partial F}{\partial v_j}\frac{\partial^2 v}{\partial m_j^2} > 0 \qquad (3a)$$

$$\text{or} \quad \frac{\partial^2 F}{\partial m_j^2} = \frac{\partial}{\partial m_j}\left(\frac{\partial F}{s_j}\frac{\partial s}{\partial m_j}\right) = \frac{\partial^2 F}{\partial s_j^2}\left(\frac{\partial s}{\partial m_j}\right)^2 + \frac{\partial F}{\partial s_j}\frac{\partial^2 s}{\partial m_j^2} > 0 \qquad (3b)$$

where v and s are written v_j and s_j where necessary to indicate that the amount of the *j*th component is the only independent variable. We can consider $\partial F/\partial s_j$

---

[1] This free energy may be either one of the two free energies, called respectively A and F by Lewis and Randall in "Thermodynamics and Free Energy of Chemical Substances", p. 155, for it will be observed that the changes we deal with are the same in both, not involving the part wherein they differ at all. It must be borne in mind that Lewis and Randall's P is the external pressure, while the p we later use is the excess pressure in the drops due to surface effects.

as the surface tension corresponding to the *j*th component and $\partial F/\partial v_j$ as the pressure p_j due to this surface tension. There seems to be no need for the various surface tensions and pressures for different components to be equal.

If the jth component has constant partial volume, $\partial v/\partial m_j$, the last term in (3a) drops out and since $\left(\frac{\partial v}{\partial m_j}\right)$ is positive the inequality becomes

$$\frac{\partial p_j}{\partial v_j} > 0 \tag{4}$$

Now in order to have stability we must have the solubility of a particular component in a drop increasing when the amount of it accidentally increases and decreasing when it decreases, otherwise large drops would get larger and small drops smaller, so they would continue to diverge in size. So the above equation states in effect that if the component is incompressible or nearly so its solubility increases with the "pressure".

No such simplification is possible with (3b) which explains why we would rather talk in terms of pressure and volume than surface and surface tension.

We can also imagine our changes to take place so that no change in composition occurs. If we let F be the free energy of a drop referred to a standard state as above, *m* the *total* mass of a particle, *v* its volume, *s* its surface, γ its surface tension, and *p* its pressure, then the same reasoning as applied before, remembering that all differentiations are to be taken with composition constant, will lead to inequalities like (3a, b), thus:

$$\frac{\partial p}{\partial v}\left(\frac{\partial v}{\partial m}\right)^2 + p\frac{\partial^2 v}{\partial m^2} > 0 \tag{5a}$$

$$\frac{\partial \gamma}{\partial s}\left(\frac{\partial s}{\partial m}\right)^2 + \gamma\frac{\partial^2 s}{\partial m^2} > 0 \tag{5b}$$

and for the incompressibility the inequality

$$\frac{\partial p}{\partial v} > 0 \tag{6}$$

p and γ are now what are ordinarily considered the "real" pressure and "real" surface tension, respectively. In this case it would be almost inconceivable for inequalities (5a, b) not to hold if (6) does, in the light of the explanation following (4), for we could scarcely imagine a decrease of fugacity of any component accompanying an increase of pressure without change in composition.

It will be noticed that the requirements for stability are such that they will be met in general by a continuous range of sizes. We are therefore prompted to look for sizes of permanent stability, but first we must consider the case where we have several sizes in equilibrium. We will assume incompressibility. We have, for transfer of the *j*th component, since $p_{j1} = \partial F/\partial v_{j1}, \ldots$

$$\Sigma\delta F = p_{j1}\Sigma\delta v_1 + p_{j2}\Sigma\delta v_2 + \ldots + \tfrac{1}{2}\partial p_{j1}/\partial v_j\,\Sigma(\delta v_1)^2 + \tfrac{1}{2}\partial p_{j2}/\partial v_j\,\Sigma(\delta v_2)^2 + \ldots \tag{7}$$

where the subscripts 1, 2,... refer to the different sizes, and where we have taken such things as we may out of the summations, and where each summation is to be taken over all particles of the proper size. The first order terms must add to zero (adding together all the first order summations), the sum of the second order parts must be positive. The δv's are arbitrary, subject only to the condition $\Sigma\delta v_1 + \Sigma\delta v_2 + \ldots = 0$. Hence

$$p_{j1} = p_{j2} = \ldots . \qquad (8)$$

Again the arbitrariness of the δv's and the positiveness of their squares necessitates for stability

$$\frac{\partial p_{j1}}{\partial v_j} > 0, \ \frac{\partial p_{j2}}{\partial v_j} > 0, \ldots . \qquad (9)$$

But even though particles of different sizes exist in equilibrium together there might be much energy released if all the particles of one size could pass over to the other size, because such a change would involve a change in the number of particles, and would involve the free energy of building up or removing whole particles. On account of something analogous to an energy of activation the change might be slow, or the system might be going over to some still more stable state. That two sizes which exist in equilibrium should have the same energy content per unit mass is an extremely improbable circumstance. We are justified, then, if, in our considerations of permanent stability, we take into account only systems in which the drops are all of the same size.

In order to find the criterion of permanent stability we need to consider how we can go from one state of temporary stability to another by means of our standard process. We will have the material of each of the particles simultaneously removed at the same rate and without change of composition, into a phase which differs only from the dispersed phase in that there is no pressure due to surface tension, till they are completely gone. We will then build up the system, creating the proper number of new particles still without change in composition, till we have put all our material back, giving a different number and a different size of drops. The particles thus formed, being of the same composition as the previous ones will not now be in equilibrium with the solution, but an infinitesimal change of composition will bring them into equilibrium. The free energy change involved will be a second order infinitesimal, if the change of the mass of the particles between initial and final states is a first order infinitesimal, as it is a change to equilibrium. But the work done in the whole change from one state to the other will later appear to be in general of the same order of magnitude as this difference of mass, and in order to find the position of maxima or minima of free energy we may set it equal to zero to the first order, neglecting the work done in the final change which gives equilibrium in composition.' We must use great caution in *distinguishing* between maxima and minima, for that involves the second order terms.

If there is an appreciable amount of surface layer which is different from the rest of the particle we will not consider it to be part of the particle, but will allow it to change so as to be in equilibrium with the liquid, and as it is always maintained at equilibrium these changes may be neglected also, as we will show. Now we are considering intermediate steps in our process. Say we remove a small part of each of our drops to our standard phase, making them all smaller in size. We did an amount of work in this process which is of the order of magnitude of the mass removed, while the work involved in reversible changes which bring the surface into equilibrium with the solution is again a second order infinitesimal. If we did not allow this change in the surface layer we see that as the particle got smaller and smaller the surface layer would get thicker and thicker, and finally when all the interior of the particle was gone we would be confronted with the problem of removing this surface part and redistributing it among a different number of particles. Our final result would, of course, be the same. I believe that the process chosen is as simple as any that may be found—in the light of the above two paragraphs we see that it requires only that we calculate the work due to surface tension involved in removing and adding material in the drops without change in composition. The difficulty is in knowing the surface tension or the pressure in the drops under the unnatural conditions used. We will be led, however, to certain approximations, and will obtain a perspective which will enable us to estimate the range of their validity.

Let us start with some particular size in which the particles all have a mass *m*. Let F be the free energy which is *lost* by one particle when all of its material is transferred as part of our process to the standard state described (it is then the free energy gained in the reverse process), and let F′ be the free energy *gained* when a particle is regenerated by this process to a mass m′ which it has in an adjacent state, or rather which it would have were it not for the subsequent transfer of material which is necessary to get back to equilibrium. The total free energy lost by removing all the drops is $\Sigma F = \Sigma (F/m) m$ where the summation is taken over all the particles. As F and *m* are the same for all particles this may be written $F/m\ \Sigma m$. Similarly the total free energy gained in the particles' regeneration is $F'/m'\ \Sigma m'$, where the summation is again taken over all the particles, there being now a different number of them. The total change in free energy, which we may denote as $\delta\Sigma F$ is given by

$$\delta\Sigma F = F'/m'\ \Sigma m' - F/m\ \Sigma m$$

But as $\Sigma m = \Sigma m'$ we get letting $F'/m' - F/m = \delta\,(F/m)$ and $m' - m = \delta m$

$$\delta\Sigma F = \left(\delta \frac{F}{m}\right) \Sigma m = \left[\frac{\frac{\partial F}{\partial m}}{m}\,\delta m - \frac{F}{m^2}\,\delta m\right] \Sigma m \text{ (to the first order).}$$

Hence as a necessary but not a sufficient condition for permanent stability

$$\frac{\frac{\partial F}{\partial m}}{m} - \frac{F}{m^2} = 0 \qquad (10)$$

where it is understood that all the differentiations are taken with constant composition, as explained.

Now $\partial F/\partial m$ may be separated into two parts. When a single particle is removed by our process a certain amount of work is done. Now suppose we change the number of particles, and regenerate them till each has a mass equal to that it had in the *initial* state. The work to regenerate each particle to this mass might be different from that it did in being removed, due to the effect of the different number of particles. We will designate this difference as $\left(\frac{\partial F}{\partial m}\right)_1 \delta m$, δm having the meaning of the previous paragraph. *Now* in order to get to the proper final state a certain amount of material must still be removed or added, and this work, done against the pressure due to surface tension and depending on the volume change in this final process, we will call $\left(\frac{\partial F}{\partial m}\right)_2 \delta m$, so $\frac{\partial F}{\partial m} = \left(\frac{\partial F}{\partial m}\right)_1 + \left(\frac{\partial F}{\partial m}\right)_2$ while $\left(\frac{\partial F}{\partial m}\right)_2 = p\frac{\partial v}{\partial m}\cdot$ It is now to be noted that in systems where the density of colloid particles is very small $\left(\frac{\partial F}{\partial m}\right)_1$ tends to vanish, while $p\frac{\partial v}{\partial m}$ remains finite. Hence for dilute colloidal solutions the necessary condition for permanent stability becomes

$$\frac{p}{m}\frac{\partial v}{\partial m} - \frac{F}{m^2} = \frac{p}{m}\frac{\partial v}{\partial m} - \frac{\int_0^v p dv}{m^2} = 0 \qquad (11)$$

In this case and in all others (unless specifically noted to the contrary) all quantities which appear under the integral sign are to be considered as functions of the variable of integration, and when they appear outside the integral sign they have the values corresponding to the upper limit.

We now turn to the consideration of other necessary conditions. In the first place our point must be a point of minimum, not maximum, free energy. This being the case the derivative of the expression $\frac{\partial F/\partial m}{m} - \frac{F}{m^2}$ with respect to the number of particles must be negative. The negative sign is explained if we consider, for example, a state in which the number of particles is *smaller* than in the critical maximum or minimum state. This means the particles are arger. They must have a tendency to become smaller if the critical point is to be a stable point. But they tend to get smaller $\frac{\partial}{\partial m}\left(\frac{F}{m}\right)$ or $\frac{\partial F \partial/m}{m} - \frac{F}{m^2}$ is positive, and so has *increased* from its zero value at the critical point. This derivative must include changes due to changes in composition, as these cannot be ignored in considerations where second order differentials enter.

For one particular case, when the dispersed and dispersing phase are practically mutually insoluble, as regards all their components, there is no appreciable change in composition, and dm/dn, where *n* is the number of particles, is a negative constant. In this case we can differentiate with respect to *m* and our condition becomes

$$\frac{\partial\left(\frac{\partial F/\partial m}{m} - \frac{F}{m^2}\right)}{\partial m} = \frac{\frac{\partial^2 F}{\partial m^2}}{m} - 2\,\frac{\frac{\partial F}{\partial m}}{m^2} + 2\,\frac{F}{m^3}$$

$$= \frac{\frac{\partial^2 F}{\partial m^2}}{m} - \frac{2}{m}\,\frac{\partial\left(\frac{F}{m}\right)}{\partial m} = \frac{\frac{\partial^2 F}{\partial m^2}}{m} > 0 \qquad (12)$$

$\frac{\partial(F/m)}{\partial m}$ being, of course, zero at a maximum or minimum. For the particular case considered the criterion (5a, b) becomes the same as this. Hence the conditions for temporary stability coupled with (10) are both sufficient and necessary for permanent stability.

For incompressibility $\partial v/\partial m = v/m$ and (11) and (12) become (multiplying through by $(m/v)^2$ and $(m/v)^3$ respectively)

$$\frac{p}{v} - \frac{\int_0^v p dv}{v^2} = 0 \text{ and } \frac{\partial p/\partial v}{v} > 0 \qquad (13) \text{ and } (14)$$

Recapitulating, these hold (1) if the particles are incompressible, (2) if the density (number per unit volume) of particles is so small that the condition of any one of them is independent of their number, and (3) if the dispersed and dispersing regions are mutually insoluble. The last of these assumptions removes the difficulty, of which we previously spoke, of evaluating γ and p under the unnatural conditions of our process. For no matter what system we consider, provided only the dispersed regions and dispersing phase separately have definite proportions of their particular components, when we arrive at a certain size drop in the course of our process it has a certain composition, which is indeed the only one any drop in that set of systems can have, and with assumption (2) above granted we can say that the surface tension of a drop depends, for a whole series of systems which satisfy the condition outlined, only on its size. Insofar as this is not true (13) will give incorrect results; and as (13) itself is an approximation from (11) this is another source of error. We have already noted that if (6) or (14) hold it is almost inconceivable that (5a, b) or (12) should not, but the validity of (12) as a condition for *permanent* stability rests on the assumption of insolubility. If this assumption is not correct it might have the peculiar effect of causing us to make a mistake in deciding whether (13) represents a maximum or minimum of free energy

Tolman[1] takes as his criterion of (presumably permanent) stability for the ideal case considered $\frac{\partial\left(\frac{\partial F}{\partial m}\right)}{\partial\left(\frac{\partial s}{\partial v}\right)} = 0$. As $\frac{\partial s}{\partial v}$ is a function of m this amounts to $\frac{\partial^2 F}{\partial m^2} = 0$. Knapp[2] does a somewhat similar thing. Needless to say, I think this is wrong, and that the error is due to neglect of the fact that drop-density changes are far-reaching and profound.

Theory of Coagulation

Just how far we can apply equilibrium principles to an explanation of coagulation is perhaps to be questioned. Certainly other factors enter, but we will proceed to an investigation of our equations when the particles are large, and a discussion of our results will show, I believe, that we have at least a valuable guide.

---

[1] Tolman: loc. cit.

[2] Knapp: Trans. Faraday Soc., 17, 457-465.

First notice that if F/m and $\partial F/\partial m$ remain finite that $\frac{\partial(F/m)}{\partial m}$ vanishes when *m* is infinite. This means that energy changes in the neighborhood of *m* infinite are small, that is, if a drop is large enough, it does not greatly matter just how large it is, a well known fact. This may explain why colloids when precipitated do not come down and form one continuous mass, but stay in flocks and clumps of "small" adhering particles; which has not been offered as an explanation as far as I know, though it is always stated that "surface energy becomes important only when the surface is large." As Brownian movement ceases at something like ten thousand molecular diameters, and as this is presumably near the size where more or less rapid settling occurs, it may well be that coagulation occurs when the particles are practically infinite in size as regards energy changes, though still microscopic as regards visual observation.

Because conglomeration represents the upper limit of particle size, whether it will be stable or not depends only whether larger or smaller particles have less free energy. Hence applying the discussion preceding equation (10) for a stable conglomerate $\frac{\partial(F/m)}{\partial m}$ or m $\frac{\partial(F/m)}{\partial m}$ which is $\frac{\partial F}{\partial m} - \frac{F}{m}$ must be less than zero when *m* is large. Hereafter we will write (compare (11) and (13)),

$$p - \frac{\int_0^v p dv}{v} < 0 \qquad (15)$$

for the condition of a stable conglomerate, making all the assumptions implied therein, i.e., fairly dilute colloidal solution, incompressibility, mutual insolubility of phases.

It is not necessary, and in fact, as we shall see, impossible under the assumptions we will make for large particles to be even temporarily stable if the conglomerate is stable. We will discuss this later.

Let us consider now the case of a colloid dispersed in salt solution. It seems that by far the greater effect of the salt lies in its electrical action, and we shall attribute it all to that, assuming that γ_o, the surface tension of the colloid solvent boundary as distinct from the electrical surface tension is independent of the salt concentration, and independent of the size of the particle unless the size is small.

Let us suppose that our charged particle may be considered to approximate to an electric double layer. Let us also assume that as long as the distance between the layers is small compared with the radius *a* that both it and the surface density of charge may be considered constant for a given composition. In the range where this holds we may write for *q*, the total charge on the particle

$$q = ka^2 \qquad (16)$$

where *k* is a constant related to the surface density and depending on the salt concentration, and for Φ, the difference of potential between the drop and the solution

$$\Phi = \frac{q}{Ka} - \frac{q}{K(a+h)}$$

$$= \frac{qh}{Ka^2}, \text{ approx.} \qquad (17)$$

(neglecting *h* as compared with *a*) where *h* is the distance between the electric layers for large particles, and also depends on the salt concentration and where K is the dielectric constant.

From (16) and (17) $kh = K\Phi$ (18)

The pressure p_e due to the electric charge is given by

$$p_e = -\frac{q^2}{8\pi Ka^4} + \frac{q^2}{8\pi K(a+h)^4}$$

$$= -\frac{q^2h}{2\pi Ka^5}, \text{ approx.} \qquad (19)$$

(again neglecting h compared with a). Substituting for q from (16)

$$p_e = -\frac{k^2h}{2\pi Ka} \qquad (19a)$$

If $p_t = 2\gamma_o/a$ is pressure due to non-electrical surface tension

$$p = p_t + p_e = \frac{2\gamma_o}{a} - \frac{k^2h}{2\pi Ka} \qquad (20)$$

This holds when the particles are large. We write as a more general expression $p_e = \frac{k^2hf_2(a)}{2\pi Ka}$ and put $\gamma_o = \gamma_o^\infty f_1(a)$, where γ_o^∞ is the non-electrical surface tension of a large drop, and assume as an approximation which certainly will not affect the general character of our results that $f_1(a)$ and $f_2(a)$ are independent of *k* and *h*. Then, remembering that *k* and *h* are quantities belonging to large drops and are constant for any given system, and that $v = 4/3\,\pi a^3$, we have for large particles

$$p - \frac{\int^{v} pdv}{v} = \frac{2\gamma_o^\infty}{a} - \frac{k^2h}{2\pi Ka} - \frac{6\gamma_o^\infty}{a^3}\int_o^a af_1(a)da + \frac{3k^2h}{2\pi Ka^3}\int_o^a af_2(a)da$$

$f_1(a)$ and $f_2(a)$ are 1 when *a* is large, but they may vary when *a* is small. We can take account of this fact by setting $\int_o^a af_1(a)da = \int_o^a ada + c_1/6$ and $\int_o^a af_2(a)da = \int_o^a ada + c_2/6$, where c_1 and c_2 are constants, since in the range of large particles the values at the upper limit of $\int_o^a af_1(a)da$ and $\int_o^a af_2(a)da$ are equal to that of $\int_o^a ada$, while the lower limit does not vary. Making these substitutions, performing the intergations, and collecting terms we get

$$p - \frac{\int_o^a pdv}{v} = -\frac{\gamma_o^\infty}{a} + \frac{k^2h}{4\pi Ka} - \frac{\gamma_o^\infty c_1}{a^3} + \frac{k^2hc_2}{4\pi Ka^3} \qquad (21)$$

We do not know the values of c_1 and c_2, but when *a* becomes *very* large we may neglect the terms with a^3 in the denominator. We then see that if

$\frac{k^2h}{4\pi K} < \gamma_0^\infty$ (15) is satisfied and a coagulated mass is stable. Otherwise it is not.

Changing the concentration of salt might affect *h* simply due to variation in the number of ions, but we would expect its chief effect to be one on *k* due to adsorption of ions. Adsorption of ions of opposite sign would cause $k^2h/4\pi K$ to finally become smaller than γ_0^∞ and precipitation would occur. But if enough ions were added there might be reversal of the effect, there being a point where *k* and Φ would pass through zero and change in sign. Since *k* and Φ must vary in the same direction k^2h which varies as $k\Phi$ must also have the same general trend, and the three quantities will be zero together. So we see that small values of Φ will be marked by coagulation, and that there will be certain limiting values of Φ, positive and negative, between which coagulation will always occur.

If Φ exceeds this critical value we can attempt to form an idea of the relation between Φ and *a* by a setting (21) equal to zero and solving for k^2h, getting

$$k^2h = 4\pi K\gamma_0^\infty \frac{1 + c_1/a^2}{1 + c_2/a^2}$$

(Unfortunately we can get a relation between Φ and *a* only if we have one between *h* and *k*.) Since this only holds if *a* is fairly large anyhow we may perform the indicated division, neglecting higher terms, and get

$$k^2h = 4\pi K\gamma_0^\infty \left(1 + \frac{c_1 - c_2}{a^2}\right) = 4\pi K\gamma_0^\infty \left(1 + \frac{c}{a^2}\right) \qquad (22)$$

where $c = c_1 - c_2$.

If $\frac{k^2h}{4\pi K} > \gamma_0^\infty$ we see by differentiating (20) that (6), the condition for temporary stability, must hold, and (22) has a real solution if *c* is negative, and as *a* becomes great $\frac{k^2h}{4\pi K}$ approaches γ_0^∞, its limiting value. If *c* is positive there is no solution when $\frac{k^2h}{4\pi K} > \gamma_0^\infty$ in the region where the assumptions on which (21) is based hold, but there might be points of permanent stability possible elsewhere. In the one case coagulation would occur after gradual increase of the size of the drops to infinity, while in the other it is hard to tell just what would happen.

One possibility that we have quite neglected in treating of coagulation is that in a given system there should be at the same time other stable conditions possible, outside of the range of large particles. If the conditions of an experiment were not such as to exclude these possibilities anomalous results might be obtained. If (15) holds then (6) cannot, and any large drop will tend to distill into the conglomerate mass, becoming smaller itself. It may continue to do this till it disappears, or it may reach a size such that it can exist in equilibrium with a coagulated mass, the condition (8) being satisfied and (9) being satisfied for the drops. If there were a large mass of the conglomerate material we would expect it to exert a sort of stabilizing influence by maintaining the composition of the solution constant, being particularly effective if (9) held, for the particles, over a long range around the equilibrium size. Knapp[1] quotes examples which answer this description.

It should be brought to the reader's notice that $\gamma = \gamma_\circ^\propto + \frac{k^2h}{4\pi K}$ for the large particles and conglomerates we have been considering. Thus if γ is positive the coagulated mass is stable, otherwise not. This is also Tolman's conclusion, which he got by assuming the surface tension not to vary or to vary only slightly, which is essentially what we did for the case of very large particles (and only for them). But Tolman, as far as I am aware, does not point out that this entails a critical potential, nor does he have anything to indicate, as equation (22) does, that this limiting potential is approached asymptotically as a approaches infinity (if a solution of this equation is possible when γ is negative.)

Interpretation of Experiments

A critical potential below which coagulation occurs has been found by Powis in experiments with oil emulsions[2] and arsenious sulfide[3], and numerous other such cases are given by Northrup[4]. While nothing very conclusive is to be learned from the experiments, it does seem probable that coagulation is brought about by an increase in the size of the particles. Ellis[5] has measured the size of oil particles supposedly in equilibrium in solutions of various concentrations of hydrochloric acid and sodium hydroxide and has found that as the potential is lowered the size of the particle increases more and more rapidly, the increase becoming very large at a definite potential, in qualitative agreement with (22).

One difficulty in interpreting the experiments is that we are never really sure whether equilibrium is established; but even if it is not it is still very likely that the equilibrium conditions would be controlling factors in the general course of events. Even the fact that hardly any colloids keep indefinitely is not a fatal objection to the theory outlined, for while there might be very slow changes taking place which would eventually result in precipitation these can be disregarded as compared to more rapid changes of another nature, in the applications of the principles of equilibrium; and, indeed, it is generally recognized that coagulation is a different kind of thing than very slow settling. It would be quite possible, for, example, to have some very slow chemical process taking place which would alter the change on the particles; this is an explanation Northrup suggests for slow settling after an initial period of stability. While this kind of change would not affect the equilibrium at any one time, it might cause a gradual change in the equilibrium size. Of course, any colloid whose precipitation can be explained by equilibrium principles really should be a reversible colloid. Merely changing the concentration of the salt after arsenious sulfide has been precipitated will not bring it back into colloidal solution. Just why this is, is hard to say. It may have something to do with the fact that the Brownian movement is present during the precipitation process, but not after precipitation, or it may be a result of slow diffusion and hence slow establishment of equilibrium in the flocks of precipitated particles, or something else may happen to the precipitated particles. And it must be remembered that our theory refers only to spherical, hence free, particles, though how much difference this might make is hard to tell.

---

[1] Knapp: loc. cit.

[2] Powis: Z. physik. Chem., 89, 186-212 (1915).

[3] Powis: J. Chem. Soc., 109, II, 734-744 (1916).

[4] Northrup in Bogue's "Theory and Application of Colloidal Behavior", Vol. I, Chap. III

[5] Ellis: Z. physik. Chem., 80, 579 (1915).

Weiser and Nicholas[1], Burton and Bishop[2], and Bach[3] have found effects of colloid concentration on the concentration of electrolyte necessary to cause coagulation, contrary to what would be expected on our theory. It is true that sometimes there are about 100 mols of colloid to every mol of electrolyte at coagulation, so that it might be argued that the adsorption could actually change the concentration of the salt in the solution, and then besides the colloid would not be "dilute" in the sense defined, after all, and our whole treatment would be invalidated. But this should not be the case for large particles, if the adsorption is truly a surface effect, and so would not make any difference in the critical potential or concentration.[4] Powis observed his arsenious sulfide solutions[5] over a period of several months, and found, for example, that if the solution were .3 millimolal in barium chloride there was no precipitate in that time, while in a .4 millimolal solution a precipitate appeared in a day or two. The results of the others would vary with the time they let their solutions stand.[6] Also, none of the other writers ever found less salt necessary to coagulate than Powis did, except that Bach once found very slightly less, and usually they needed much more. So it seems probable that Powis was observing equilibrium effects; and the others rate of reaction effects as they, themselves, would probably agree. Powis, himself, did not come as close to

---

[1] Weiser and Nicholas: J. Phys. Chem., **25**, 742-757 (1921).

[2] Burton and Bishop: J. Phys. Chem., **24**, 701-715 (1920).

[3] Bach: J. Chim. phys., **18**, 52 (1920).

[4] In order to get some idea of the general order of magnitude of $\left(\frac{\partial F}{\partial m}\right)_1$, as used in the paragraph immediately preceding equation (11), we may note (using primes to distinguish the variables in the integration from their values at the upper limit, as confusion might arise in this case) that (for incompressibility)

$$\left(\frac{\partial F}{\partial m}\right)_1 = \int_0^v \frac{\partial p'}{\partial v}\,dv' = \frac{d}{dv}\int_0^v p'dv' - p \quad (23)$$

But $p = \frac{2\gamma}{a}$, and if, for large values of a, γ is approximately constant(which is the case if the adsorption is truly a surface effect, for then, for large values of a the adsorption should not be able to appreciably change the concentration of salt in the solution). $\frac{d}{dv}\int_0^v p'dv' = \frac{2\gamma}{a}$ so $\left(\frac{\partial F}{\partial m}\right)_1$ obviously becomes zero faster than p, as is seen by putting these values, which become more and more approximately correct as a becomes large, in (23).

[5] Powis: J. Chem. Soc., **109-2**, 734-744 (1916).

[6] See Weiser and Nicholas: loc. cit. (page 750).

observing equilibrium effects as he might have, as he did not consider precipitation to have taken place till the concentration of the barium chloride was .5 millimolal, but the only effect this can have is to cause the measured magnitude of the critical potential to be slightly too low.

Summary

The phase rule has been deduced in a form in which it can be directly applied to colloids, and by its use it has been inferred that both where the particles are electrically charged and where they are not that equilibrium exists only if the particles are all of one size, or of a few definite sizes.

The stability of the equilibria has been examined, and two distinct types of stability, temporary and permanent, have been found. The conditions for stability, and the relation between the two kinds of stability have been considered in detail.

These considerations have been applied to coagulation, and an attempt has been made to interpret experiments with their aid.

I wish to thank Professor R. C. Tolman of the California Institute of Technology and Professor J. H. Hildebrand of this laboratory for valuable suggestions.

Department of Chemistry,
University of California,
Berkeley, California.

ANTIMONY SULPHIDES

BY LAUCHLIN MACLAURIN CURRIE

I. Composition of the Antimony Sulphides

Stibnite was known five centuries ago, and recognized as a mixture or combination of sulphur and antimony[1]. It was in 1812 that Davy[2] first showed by analyses that stibnite is the trisulphide of antimony, and corresponds to the formula Sb_2S_3. The quantitative study of the antimony sulphides really began with Davy's work. Others followed closely behind him.

Faraday[3] supposed that he had prepared the disulphide. Unger[4] claimed to have prepared a disulphide according to the reaction $3Sb_2S_3 = Sb_2S_5 + 2Sb_2S_2$. This so-called disulphide was never separated. Dammer[5], Pélabon[6], and Moissan[7] all agree that the existence of such a compound is very unlikely. Gmelin-Kraut[8] states that a sulphide containing less sulphur than that required by the formula Sb_2S_3 does not exist.

H. Rose[9] concluded that from a solution of antimonic acid a mixture of trisulphide of antimony and sulphur would be thrown down by H_2S. Bunsen[10] disagreed and recommended the precipitation of antimony as the pentasulphide for the quantitative estimation of the element. Neither Willm[11], Mourlot[12] nor Thiele[13] could check with Bunsen's work. All found that the sulphide as precipitated contained sulphur easily extractable with a sulphur solvent. Bosek[14] did much towards clearing up the question, by showing that only if Bunsen's directions are carefully followed will pure pentasulphide be formed. He also made a study of the factors affecting the reaction.

Berzelius[15] in 1822 stated that antimony tetrasulphide could be prepared by passing hydrogen sulphide through a solution of Sb_2O_4. Since that time there has been much discussion as to the existence or non-existence of the tetra- and penta-sulphides of antimony. Considerable work has been done but relatively little since that of Klenker[16] who left the question far from settled.

---

[1] Abegg: "Handbuch anorg. Chem." **3** III, 573, 596 (1907); Mellor: "Modern Inorganic Chemistry", 607 (1917).

[2] Phil. Trans., **1812**, 196.

[3] Pogg. Ann. **23**, 314 (1831).

[4] Arch. Pharm. (2) **147**, 193 (1871); **148**, 2 (1871).

[5] Dammer: "Handbuch anorg. Chem." **2** I (1) 213 (1894).

[6] Compt. rend., **130**, 911 (1900); Chem. News, **81**, 202 (1900).

[7] Moissan: "Traité de Chimie minerale," **2**, 42 (1905).

[8] Gmelin-Kraut: Handbuch anorg. Chem., **3** II, 698 (1908).

[9] Pogg. Ann., **107**, 186 (1859).

[10] Ann., **192**, 305, 317 (1878).

[11] Z. anal. Chem., **30**, 428-443 (1891).

[12] Compt. rend., **123**, 54-55 (1896).

[13] Ann., **263**, 371 (1891).

[14] J. Chem. Soc., **67**, 515 (1895).

[15] Schweigger's J., **39**, 58 (1822).

[16] J. prakt. Chem., (2) **59**, 150, 353 (1899).

The object of this study was two-fold: (1) the determination of the nature and number of phases in so-called antimony pentasulphide; (2) the study of the colors of antimony sulphides—particularly the trisulphides—and the factors affecting the colors.

Antimony pentasulphide is referred to here as "so-called", meaning, in this case, any substance that on analysis gives 60% antimony and 40% sulphur. One may easily calculate that this might be a trisulphide plus 16% excess sulphur, a tetrasulphide plus 8% excess sulphur, a pure pentasulphide, or a mixture of the three sulphides plus the required amount of excess sulphur.

Analytical methods alone can tell one little as to the composition of such a substance; a mixture of 0.840 gm. of stibnite plus 0.160 gm. of sulphur will on analysis show exactly the same composition as will pure pentasulphide, or a mixture of 0.420 gm trisulphide, 0.460 gm tetrasulphide plus 0.120 gm of sulphur.

Most of the early research, taking note of the effect of different sulphur solvents on the sulphides, was done with especial care to note the exact amount of sulphur extracted under definite conditions, and the exact composition of the resulting residue. Early workers carefully noted the *amount* of sulphur extracted, but failed to get any idea as to the *way* in which sulphur was extracted, and so failed to distinguish between sulphur present in the original sample as a separate solid phase and that formed by subsequent decomposition of the sample.

The method as adopted for this study is not a new one. It has been used successfully by Allen[1], Foote[2], Thiel[3], Miller and Kenrick[4], and others. It is based on the variation in concentration of a solution in equilibrium with a solid phase of varying composition. When concentration of solution is plotted against composition of the total solids, the resulting curve will give an idea as to the nature of the material studied.

The problem here studied differs radically in one important detail from the work mentioned above. All the work required that equilibrium be reached. The previous studies dealt with reversible equilibrium, where the equilibrium may be reached by approach from either direction. In the problem here studied, equilibrium could be reached from one direction only, the side corresponding to the higher sulphide.

The study is, therefore, one of an irreversible equilibrium. Just why this should be true is by no means clear. To date, however, all attempts to replace sulphur after removal from a sulphide have resulted in failure.

The method as usually used calls for the treatment of the sample with successive portions of solvent, allowing sufficient time to reach equilibrium, and determining the composition of the solid and solution phases. In this case, the method was changed to suit the problem. In the first place, instead of treating the same sample with successive portions of solvent, equal samples were treated with increasing amounts of solvent, allowed to reach equilibrium, and the composition of the two phases determined. This method was found to be much faster, allowing the study of several samples at one time. Other factors also influenced our choice of this method. In the repeated treatment of the same small sample, errors are cumulative and so soon tend to equal the changes in results due to natural causes. The use of volatile solvents—and most sulphur solvents are quite volatile—necessitates rapid handling, and any loss of solvent in handling introduces appreciable error into the calculation of results.

---

[1] Am. Chem. J., **25**, 307 (1901).

[2] Am. Chem. J., **29**, 203; **30**, 339 (1903); 32, 246, 251 (1904).

[3] Z. physik. Chem., **43**, 641 (1903).

[4] J. Phys. Chem., **7**, 259 (1903).

The results as obtained by treating equal samples with increasing amounts of solvent, were calculated back to the same basis as though obtained by repeated treatment of the same sample with small amounts of solvent.

It is possible in this way to show that true antimony pentasulphide may, under certain conditions, be prepared pure, but as ordinarily made it consists of a mixture of antimony pentasulphide, antimony trisulphide, and sulphur. It was also found that the so-called antimony pentasulphide, as prepared by decomposing thioantimonates with dilute acids, is a mixture of free sulphur and a solid solution of sulphur in antimony tetrasulphide. Both tetra- and pentasulphides of antimony were found to be decomposed by heating, breaking down finally to antimony trisulphide and sulphur.

Method of Procedure:

The sample was weighed into a tared test tube. Varying quantities of the solvent chosen were added to the test tube containing the sample of sulphide, and the amount determined by weighing tube and contents. This was then allowed to stand at the temperature chosen, with shaking at frequent intervals, until equilibrium was reached.

When equilibrium was reached, the contents of the tube were allowed to settle as much as they would, and the supernatant liquid transferred to centrifuge tubes, care being exercised to prevent losses of solvent by evaporation, tubes being immediately corked tightly. The centrifuge tubes were then centrifuged until perfectly clear, the liquid transferred to a weighed weighing bottle, and weighed. The solvent was then evaporated from the solution at a temperature of less than 80°C. The amount of sulphur in the sample of solution taken was then determined by weighing the weighing bottle and crystallized sulphur to constant weight.

This method for determining sulphur was chosen after considering several others. It was found superior to weighing the sulphide before and after extracting and calculating the sulphur by difference. This latter method has the disadvantages of including in the sulphur so determined any other soluble compounds, any moisture in the sample, and errors due to loss of material. Calculations of the amount of sulphur removed, by determining the increase in the percentage of antimony in the sulphide, gave too widely varying results for small amounts of sulphur removed. Determination of removed sulphur by calculation after converting sulphur to barium sulphate was used in a few cases only.

Drying and weighing the dissolved sulphur was found to be comparatively rapid, and accurate enough for the purpose. Sulphur has such a low vapor pressure at the temperatures used that its loss is negligible[1]. Samples were dried to constant weight in three hours or less. Continued heating for a second three-hour period showed losses of sulphur averaging less than half percent of the sulphur weighed.

This procedure will hereafter be referred to as our standard procedure.

In the experimental part of this work, samples of antimony sulphides were prepared by several different methods, and the composition of the different samples determined. All the samples on analysis showed very close agreement with the theoretical analysis of pure pentasulphide, 60% Sb, 40% S.

The samples prepared by different methods and under different conditions showed very different properties, and compositions. These will be taken up in detail under separate heads.

Pure Pentasulphide

Experimental:

Bunsen's method[2] was followed in the preparation of a supposedly pure pentasulphide. (Compare also Bosek[3], and Klenker[4].) The precipitate was filtered out, washed with water, alcohol, carbon disulphide and alcohol, then dried in a vacuum desiccator over sulphuric acid. When dry the resulting pigment was thoroughly mixed, sampled and analyzed.

Analysis: Pigment 7.

Antimony	60.05%
Sulphur	39.41%
Moisture	0.38%
Chlorides	0.08%

Color: Good rich orange.

This analysis shows that the sample corresponds to that of an antimony pentasulphide slightly deficient in sulphur. Refluxing samples of this pigment with chloroform and carbon disulphide for three hours removed 10.1 and 12.6 mg of sulphur per gram of sample. Standing in these solvents for three weeks at room temperature, samples showed losses of 0.0 and 0.9 mg respectively, proving that there was practically no free sulphur in the substance.

Concentrated HCl liberated sulphur equivalent to 16.02 percent by weight. (Theoretically only 15.39%. Difference is probably due to occluded salts.)

Heating this pigment showed little visible effect until temperatures around 100°C. were reached, when a dulling of the color was noted. At 135° the pigment had darkened appreciably to a brown, and at 150°C. traces of black color appeared.

---

[1] Jones: J. Soc. Chem. Ind., **31**, 815 (1912); Luff and Porritt: **40**, 275T (1921).

[2] Bunsen: Ann., **192**, 305, 317 (1878).

[3] J. Chem. Soc., **67**, 519 (1895).

[4] J. prakt. Chem., (2) **59**, 150, 353 (1899).

This sample was used for subsequent work as a pure pentasulphide.

In order to determine the exact composition of this pigment the effect of sulphur solvents was tried in several ways and over a long period of time.

The results of these tests may be summed up as follows:

Cold carbon bisulphide, chloroform, carbon tetrachloride, benzene, and toluene have practically no effect on pure pentasulphide. These same solvents at their boiling points have slightly more effect—particularly the carbon bisulphide. Boiling acetone has but slight effect, although it has a higher boiling point than the bisulphide.

Samples of the pentasulphide when heated as a dry powder to temperatures above 75°C., showed larger amounts of sulphur dissolved. A sample heated above 157°C for three hours lost 15.51% by weight to CS_2, the residue after extraction analyzing pure trisulphide.

From the work done on this material, it is reasonable to conclude that:

(1) Antimony pentasulphide unquestionably exists.

(2) The pentasulphide decomposes on heating, liberating sulphur.

(3) It is practically unaffected by cold sulphur solvents, and but slightly so by the hot solvents.

(4) The effect of hot carbon bisulphide is due to the higher temperature of the boiling solvent, and also to the very great solubility of sulphur in this solvent. The statement of Esch and Balla[1] that only impure carbon bisulphide affects antimony pentasulphide could not be substantiated. The further the concentration of the sulphur in solution from the saturation value, the lower its potential and the greater the power of the solvent to decompose the sulphide[2].

So-called Pentasulphide

In order to test the so-called antimony pentasulphide, samples of pigment were made by passing a stream of hydrogen sulphide through solutions of pentavalent antimony.

The conclusions of Bosek[3] were verified. Some of the pentavalent antimony is reduced, evidently to the trisulphide direct, and sulphur is liberated. Long continued passage of the current of H_2S, high temperatures, and low acid concentrations were found to favor the formation of the trisulphide. At temperatures above 95° the precipitate was largely trisulphide. A sulphide precipitated by a slow stream of H_2S, passed for 5 hours through a boiling antimonic chloride solution, filtered, washed with water, alcohol, carbon bisulphide, and alcohol, then dried in a vacuum desciccator, showed on analysis 69.06% antimony. This corresponds to a maximum of 8% antimony pentasulphide in the mixture.

---

[1] Esch and Balla: Chem. Z., **28**, 595 (1904).

[2] Cf. Weber: "Chemistry of Rubber", 186 (1906); Luff and Porritt: J. Soc. Chem. Ind., **40**, 275T (1921).

[3] J. Chem. Soc., **67**, 526 (1895).

Treating pure antimony pentasulphide with successive portions of solvent show that, after the extraction of a *very* small amount of sulphur, the concentration of the sulphur in solution on further treatment drops to zero. This result agrees with that obtained by Hutin[1] and Dubosc[2]. Pure pentasulphide is practically unaffected by the solvent.

The so-called antimony pentasulphide behaves entirely differently with reference to the solvent. Some sulphur is dissolved, giving a solution saturated with sulphur. See Fig. 1. Further treatment with solvent extracts more sulphur, the concentration remaining constant—saturated solution—until all the sulphur as a separate solid phase disappears. The concentration of sulphur in the solution then drops to zero. The position of the break depends upon the method used in preparing the sample of pigment. Curves "efg", "efcd", and "efchi" on Fig. 1 show diagrams of three different samples. These samples are considered mixtures of the penta- and trisulphides with some sulphur. Sloping lines in place of lines "fg" and "hi" would indicate the existence of solid solutions, while vertical lines as obtained might be taken to indicate definite compounds. Line "cd" would indicate the presence of antimony tetrasulphide. But since the drop from the saturation value of sulphur in solution to a zero value is practically vertical, and since the positions of the breaks and lines "fg", "cd", and "hi" may be altered almost at will by changing conditions of precipitations, one is safe in assuming that the residue in each case is simply a mixture of the penta- and trisulphides and not a single compound or solid solution. The curve "efcd" indicates that the residue was composed of equal parts of penta- and trisulphide.

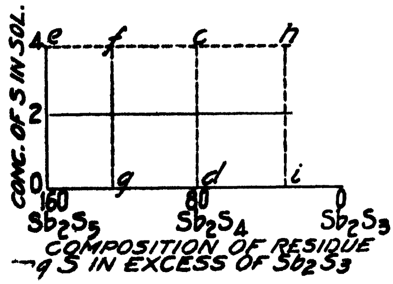


Fig. 1

Mixed Sb_2S_5, Sb_2S_3 and S

Sulphides from Thioantimonates.

The next group of sulphides studied was that made by decomposing thioantimonates with acids. The equation for this reaction is usually written

$$2Na_3SbS_4 + 6HCl = Sb_2S_5 + 6NaCl + 3H_2S$$

The study of this group showed that actually the reaction does not give pure pentasulphide, but always gives more or less free sulphur. The object of this study was to determine the composition of the other solid phase or phases.

Pure sodium thioantimonate (Baker and Adamson's C. P.) was recrystallized and dissolved in cold water, 85 grams of the salt per liter of water. The thioantimonate was then decomposed by dilute acid solution, thoroughly cooled. The acid concentration used was less than 5%. In all cases the resulting precipitate was washed by decantation, filtered, washed well with water and alcohol, and thoroughly dried. Several samples were made with slightly varying conditions. Of these, the following are typical.

---

[1] Ann. chim. anal., 21, 32 (1916).

[2] Le Caoutchouc et la Gutta Percha, 8886, 8958 (1916).

Golden 3. Dilute sulphuric acid poured into thioantimonate solution. Washed precipitate dried at 105°-110°. Yield of approximately 96% of theoretical value. Color—rather dull orange.

Golden H. Using dilute HCl. Excess H_2S removed by slow stream of air. Dried at less than 70°C. Yield 95% of theoretical. Color—good rich orange.

Golden A. Same as Golden H, except that excess H_2S was not removed by air, and a temperature of less than 55°C. was used. Yield 97% of theoretical. Color—good rich orange.

Golden B. Exactly same as Golden A, except for the fact that the thioantimonate solution was poured into the acid, rather than the acid into the thioantimonate solution. Dried in the same way as Golden A. Gave same yield. Color—slightly darker than Golden A.

Golden D. Exactly same as Golden A, except temperature of drying. The washed filter cake was dried in a vacuum desiccator over sulphuric acid. Required 23 days to get the moisture content less than half of one percent. Color—rather dull tan.

The analyses of these samples were as follows:

	Golden 3	Golden H	Golden A	Golden B	Golden D
Antimony	59.60%	59.2%	59.84%	59.51%	59.59%
Sulphur	40.5	40.8	39.96	40.17	39.75
Moisture	0.16	0.04	0.39	0.32	0.47
Chlorides	trace	trace	———	———	trace
Excess S	0.76%	1.34%	0.06%	0.50%	0.04%

The excess sulphur was figured from the antimony content on the dry basis.

The above listed samples were treated with a solvent according to our standard method of procedure. All the data in Tables I-IV are calculated on the basis of one gram sample of sulphide used. The solvent chosen for this set of experiments was a mixture of two parts by weight of chloroform to one of acetone, giving a mixture of specific gravity 1.256 at 23°C.

TABLE I Golden 3. FIG. 2.

Solvent added grams	Sulphur removed milligrams	Conc. of S in soln.	Analysis of residue: mg S in excess of Sb_2S_3
0.0	0.0	0.0	167.6
4.6	17.5	3.81	150.1
1.4	5.2	3.72	144.9
3.5	12.5	3.57	132.4
5.5	20.0	3.64	112.4
8.5	19.8	2.33	92.6
6.5	7.0	1.07	85.6
14.5	2.6	0.18	83.0
64.0	1.4	0.02	81.6

TABLE II. Golden H. FIG. 3.

Solvent added grams	Sulphur removed milligrams	Conc. of S in soln.	Analysis of residue: mg S in excess of Sb_2S_3
0.0	0.0	0.0	173.4
6.27	23.2	3.70	150.2
2.70	10.1	3.74	140.1
3.63	13.4	3.69	126.7
6.4	22.1	3.45	104.6
2.9	8.2	2.83	96.4
3.4	9.2	2.71	87.2
5.9	7.8	1.32	79.4
16.4	1.0	0.06	78.4

TABLE III. Golden A. FIG. 4.

0.0	0.0	——	
4.74	17.2	3.62	160.4
0.99	3.6	3.64	143.2
3.52	12.7	3.60	139.6
4.25	14.5	3.41	126.9
1.50	4.7	3.15	112.4
12.0	20.3	1.70	107.7
3.1	3.7	1.20	87.4
20.8	4.5	0.21	79.2
20.7	0.2	0.00	79.0

TABLE IV. Golden B. FIG. 5.

Solvent added grams	Sulphur removed milligrams	Conc. of S in soln.	Analysis of residue: mg S in excess of Sb_2S_3
0.0	0.0	——	165.0
5.45	19.6	3.60	145.4
3.83	14.2	3.70	131.1
5.3	16.4	3.10	114.7
2.95	7.7	2.61	107.0
15.7	14.1	0.90	92.9
14.6	5.3	0.36	87.6
12.1	0	0.0	87.4

The data for these samples of sulphides are perhaps best understood when considered from their graphical statements. All four of these samples have some noticeable points in common.

All four samples show that the concentration of sulphur in solution remains constant for a certain length, then the concentration decreases more or less abruptly, and in all the cases approximates a zero concentration when the composition of the solids is equivalent to that of antimony tetrasulphide.

The fact that the concentration of sulphur in solution remains constant indicates that there are two solid phases present. The fact that this constant concentration represents the solubility of sulphur, indicates that sulphur is one of these two phases. When the concentration of sulphur begins to decrease, one is safe in concluding that a solid phase has disappeared.

If the remaining total solids were antimony pentasulphide plus some antimony trisulphide, the disappearance of the free sulphur would cause the concentration of sulphur in the next solution to fall to zero, for it has already been shown that the pure pentasulphide is not decomposed by the solvents.

With a sloping curve from the constant value down to zero at approximately Sb_2S_4, one best explains conditions by assuming the existence of a solid solution of sulphur and Sb_2S_4. In all four cases here, further treatment of sample with solvents, showed no extraction of sulphur after the composition corresponding to Sb_2S_4 was reached.

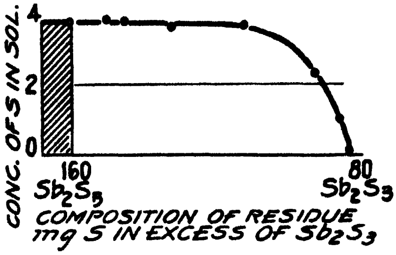


FIG. 2
Pigment Golden 3

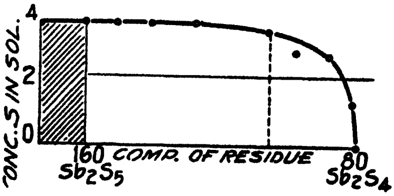


FIG. 3
Pigment Golden H

The shaded areas on the curves for Golden 3, B, and H (Figs. 2, 5 and 3) show presence of sulphur in excess of that required by pure antimony pentasulphide. This sulphur may have come from either of two sources: the recrystallized thioantimonate may have occluded some excess sulphur, or sulphur may have been formed by the oxidation of the hydrogen sulphide given off in the decomposition of the thioantimonate. This latter is much more likely to be the true explanation for the recrystallized thioantimonate gave clear crystals, which showed on analysis an antimony content of 25.00% and 24.97%. The theoretical value is 25.04%. The fact that removing the excess hydrogen sulphide with a stream of air, as in the case of Golden H, also showed a larger excess of sulphur, further confirms the statement that the hydrogen sulphide is the source of most of the excess sulphur.

The analysis of Pigment A corresponds to that of a pure antimony pentasulphide. These data, however, show that this sample consists of a solid solution of sulphur and antimony tetrasulphide, with just the amount of excess sulphur to bring the analysis up to that of pure pentasulphide.

Comparison of the diagrams for Golden A and B shows a general similarity, and indicates that, in general, the phases present in the samples are the same. The position of the break in the curves show that Pigment A has a larger amount of free sulphur, as compared with the amount of solid solution. This fact may be stated in another form by saying that the solid solution formed in Golden B is richer in sulphur than the solid solution in the case of A. The different methods of preparation would account for this difference. In the case of the Golden A, pouring the acid into the thioantimonate gives a precipitate formed largely in the presence of thioantimonate in excess. When a particle of precipitate is formed, it tends to adsorb acid. When subsequently the particle is stirred through the thioantimonate solution, the adsorbed acid is neutralized by more thioantimonate and more precipitate is formed, with the evolution of hydrogen sulphide, either actually in the original particle, or in close contact with it. This hydrogen sulphide tends to reduce any of the higher sulphides of antimony (see later), thus forming more free sulphur as a separate phase.

In the case of Golden B, the particles formed still tend to adsorb acid, for acid is always in excess. But the particle is later stirred through the acid solution and no further reaction takes place, for dilute acid is always in excess.

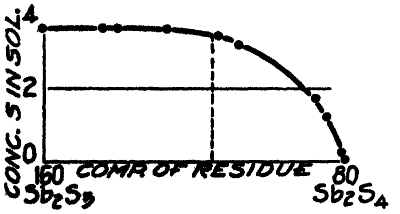


FIG. 4
Pigment Golden A

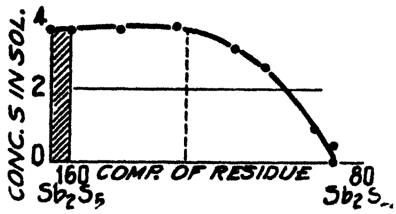


FIG. 5
Pigment Golden B

So the tetrasulphide and sulphur are formed all at the same instant, and so form a higher percentage of solid solution and less of free sulphur as a separate phase. There is a possibility that some antimony pentasulphide is formed here in small amounts. Most of it is decomposed by the hydrogen sulphide and acid, but a very small amount may remain in the material. The fact that the curve for Golden B intersects the axis of abscissae on the left side of the value corresponding to pure tetrasulphide, may be accounted for by supposing the presence of a small amount of antimony pentasulphide, which has been shown to be unaffected by the solvent used.

The difference between pigments Golden A and Golden B calls attention to the possibility of changing the composition of the solid solution formed between Sb_2S_4 and sulphur. Goldens 3, H and A show the presence of a solid solution of about the same composition in each case. This composition corresponds to that of two atoms of sulphur and five molecules of the tetrasulphide. Golden H has slightly less than this amount of sulphur: the difference may be due to decomposition of the solid solution by the passage of the stream of air. This point was checked qualitatively.

Several factors were found to affect the composition of the solid solution. Among these factors, increasing temperature of the reaction or of drying, passage of a stream of air or hydrogen sulphide, and precipitation from thioantimonate solutions containing free alkali, all showed some increase in the amount of free sulphur (present as a separate phase) formed at the expense of the sulphur in solid solution.

Curves similar to the preceding were not run on samples of Pigment Golden D. The sulphur extracted by chloroform and carbon bisulphide, refluxing three hours, amounted to 8.05 and 8.20% respectively. The residue insoluble in boiling 1:2 HCl amounted to 16.09%.

Similar treatment of Golden H gave 9.54% sulphur extractable by refluxing carbon bisulphide, and 17.2% residue with HCl.

These figures check with the conclusions drawn from the equilibrium curves. The solvents remove the sulphur present as a free solid phase, and that in solid solution with the tetrasulphide. The acid decomposes the antimony tetrasulphide, freeing any other atom of sulphur, and leaving as a residue all the sulphur in excess of that required to form antimony trisulphide. This sulphur is evolved as hydrogen sulphide.

From the above studies it may be concluded that the decomposition of sodium thioantimonate by dilute acid does not yield antimony pentasulphide, but a mixture of sulphur and a solid solution of sulphur and antimony tetrasulphide. The upper limiting composition of this solid solution corresponds approximately to the formula $Sb_2S_{4.66}$.

Trisulphide

It was considered worth while next to spend a little time upon antimony sulphides prepared from other materials.

Supposedly pure trisulphide was prepared by passing hydrogen sulphide slowly into a hydrochloric acid solution of freshly distilled antimony trichloride. A rich yellow precipitate separated. This was filtered out, washed, and dried at 105-110°C. The color of the pigment darkened a little on drying but was still a rich golden yellow. The analysis showed an almost pure trisulphide, containing but 0.6% excess sulphur. This was evidently produced by the oxidation of some of the hydrogen sulphide. When the pigment was tested with solvents, as in the case of the pentasulphides, it lost but 0.6% sulphur, checking exactly with the analyses. This sample was called Pigment E.

The formation and action of trisulphides of antimony showed nothing new nor unusual. This sample was used in work later on.

Several samples of the so-called antimony "crimson sulphide" (variously called "antimony cinnabar", "vermilion") were prepared from the interaction of a dilute solution of antimony trichloride (in hydrochloric acid) with a solution of sodium thiosulphate. The object of this set of experiments was to determine the nature of the sulphide material formed, and to study the factors affecting it.

According to Fehling[1] the interaction of trivalent antimony in dilute acid, with solutions of sodium thiosulphate, gives a pigment which is an antimony oxysulphide, and not the trisulphide. Von Szilagyi[2] agrees with this idea, but also states that some antimony pentasulphide may be formed. Bayer and

---

[1] Fehling: "Neues Handwörterbuch Chem.," **1**, 686 (1874).

[2] Z. anorg. allgem. Chem., **113**, 69 (1920).

Company[1] obtained a patent which purports to obtain some pentasulphide from this reaction. Von Hahn[2] also claims that some pentasulphide is formed. On the other hand, Baubigny[3], Dammer[4], and Gmelin-Kraut[5] state that it is the trisulphide that is formed.

Varying the conditions of precipitation were found to have marked effects on the composition and color of the precipitate. (The color effects will be taken up in detail later.) Increasing percentage of sulphur was obtained by increasing temperature of mix, by increasing percent acidity of final mix up to a certain limit (about 30%), by increasing the ratio of thiosulphate to trichloride, and by increasing the concentration of the thiosulphate solution used.

Samples of this precipitate—of varying color, and with a wide range of sulphur content (2-52%)—were tested according to our standard procedure, using the acetone-chloroform mixture. In every case of the pigments precipitated from the sodium thiosulphate and antimony trichloride solutions, they were found to consist of antimony trisulphide with free sulphur as a separate solid phase. If sufficient acid were present to prevent all hydrolysis of the antimony chloride, the analyses showed a total of 100%,—antimony, sulphur, moisture and trace of chlorides being the only substances present. No evidence was found as to the formation of any pentasulphides, oxysulphides, or solid solutions.

In order to determine what the reaction would be if antimony trisulphide were treated with sulphur at the melting point of the latter, a sample of finely divided trisulphide (pigment E) was mixed with finely ground flowers of sulphur, and the mixture heated in a test tube placed in a bath of molten sulphur, just above its melting point. The color of the trisulphide slowly deadened and darkened, finally becoming black before the sulphur in the test tube was at its melting point. The mix was held at a temperature of 124°C. for an hour, then removed and cooled slowly.

The analysis of the mix showed the composition was: antimony 61.0%, sulphur 38.78%, moisture—trace, chlorides (HCl) 0.08%.

Samples of this blackened pigment F were extracted with chloroform under the reflux condenser. 14.3 and 14.35% of sulphur were removed. Carbon bisulphide removed 14.35% sulphur. The original analysis showed that the pigment contained 14.39% sulphur in excess of the trisulphide.

Other samples of this material were tested according to our standard procedure. They showed clearly that this material consisted simply of black crystalline antimony trisulphide and free sulphur. There was no evidence of any compound or solid solution between the two.

All attempts to add sulphur (other than mechanically) to trisulphides resulted in failures. Extracted samples of pigments E and F (golden and black trisulphides, respectively) were allowed to stand in contact with solutions of sulphur solvents saturated with sulphur. The golden trisulphide (Pigment E) removed less than 0.3% of its weight of sulphur from the solution. The crystalline trisulphide did not remove a detectable amount. The sulphur removed by Pigment E was likely held by adsorption or occlusion. The samples were so finely divided that such surface effects would be easily possible. Pigment F, being crystalline, and much coarser, naturally showed less, if any, effect.

---

[1] Brit. Pat., 14355, June 19 (1912); Chem. Abs., 7, 4050 (1913).

[2] Kolloid-Z., 31, 200 (1922).

[3] Compt. rend., 119, 687 (1894).

[4] Dammer: "Handbuch anorg. Chem.," 4, 341 (1903).

[5] Gmelin-Kraut: "Handbuch anorg. Chem.," 3 II, 703 (1908).

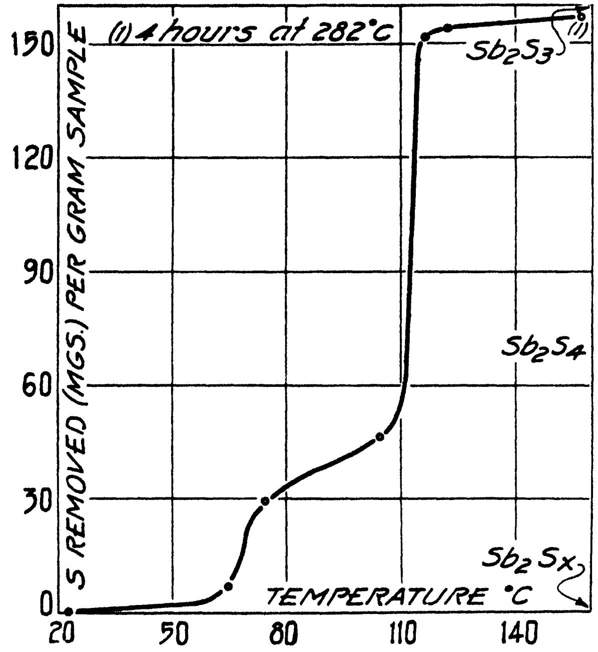


FIG. 6

Pigment 7. Heated eight hours. Effect of temperature on sulphur extracted.

Solutions nearly saturated with respect to sulphur, when in contact with antimony sulphides containing excess sulphur, remove sulphur from the sulphide up to the point of saturation of the solution. Pigments Golden 3, H, B and samples of the crimson trisulphide all showed this effect.

These few experiments showed that, if to a system of antimony sulphides, sulphur and sulphur solvent—at equilibrium conditions with the solvent saturated with sulphur—more sulphur be added, the excess sulphur is thrown out as a free solid phase, with no evidences of any addition or combination with the antimony sulphides.

The effect of the heat on the sulphides of antimony was next considered and studied. To date there has been considerable variety in the results and conclusions reached by the different investigators. Klenker's work[1] published in 1899 was very carefully performed and showed definite results, but has been rather frequently overlooked. Klenker noted that pure pentasulphide was decomposed by heat, and several of his experiments showed that temperatures of 85-90°C. were sufficiently high to give a noticeable breaking down. Von Bacho[1], von Zani,[2] Luff and Porritt[3], and many others have also given the question some consideration.

---

[1] Klenker: J. prakt. Chem., (2), 59, 150, 353 (1899).

It was thought likely that a phase rule study of the question might give some insight as to the conditions and products of the decomposition of antimony sulphides.

Samples of the pure pentasulphide were placed in carefully cleaned and dried test tubes, corked, and then subjected to heat at various temperatures for periods of eight hours each. After cooling the tubes, the samples were extracted with chloroform.

The data for these samples are shown in Table V. They are shown graphically in Fig. 6. This curve shows that the rate of decomposition is very low at low temperatures, is appreciable at temperatures around 75°C. and increases very rapidly at temperatures above 100°C. At 120°C. the decomposition is practically complete.

TABLE V. Pigment 7, Heated 8 Hours. FIG. 6.
Effect of Temperature on Sulphur extracted.
y = milligrams extracted sulphur per gram sample.

Temp.	y	Temp.	y
23° (room)	0.0	117°	152.0
65	7.0	123	154.0
75	29.8	158	156.8
105	46.6	282	161.2

The last sample was heated for four hours in an atmosphere of CO_2. The value of sulphur extractable was determined by difference, and includes any volatilized matter other than sulphur, moisture, and any oxidation.

TABLE VI. Effect of Continued Heating on Amount of Sulphur extractable from Pigment 7. FIG. 7.

Time of Heating	Temp. 65°C.	Temp. 75°C.	Temp. 105°C.	Temp. 123°C.
8 hours	7.0	29.8	46.6	154.0
24 hours	11.2	——	79.1	156
48 hours	——	48.2	——	158
5 days	——	58.0	——	——
1 week	14.1	60.2	89.1	158
2 weeks	15.0	70.0	91.0	158
3 weeks	15.4	77.2	——	——
4 weeks	——	83.3	——	——

[1] Ann. Chim. applicata, **12**, 143-152 (1919).

[2] Chem. Abs., **4**, 1947 (1910).

[3] J. Soc. Chem. Ind., **40**, 277T (1921).

Since the slope of the curve showing relative decomposition of pure pentasulphide at different temperatures is rather uncertain at temperatures below 75°C., another series was run in which samples were heated at constant temperature for different lengths of time. Series were run at temperatures of 65°, 75°, 105°, and 123°C. Data for these series are given in Table 6, and the results plotted on Fig. 7.

Continued heating at 65° (Curve D) shows a very small amount of sulphur liberated in 3 weeks by the decomposition of antimony pentasulphide. Heating at 75° (Curve C) shows a much more rapid decomposition at first, but later slows down appreciably. Sulphur corresponding to one atom per molecule of pentasulphide is rather easily extracted, indicating that the first product of the decomposition of the pentasulphide by heat may be the antimony tetrasulphide.

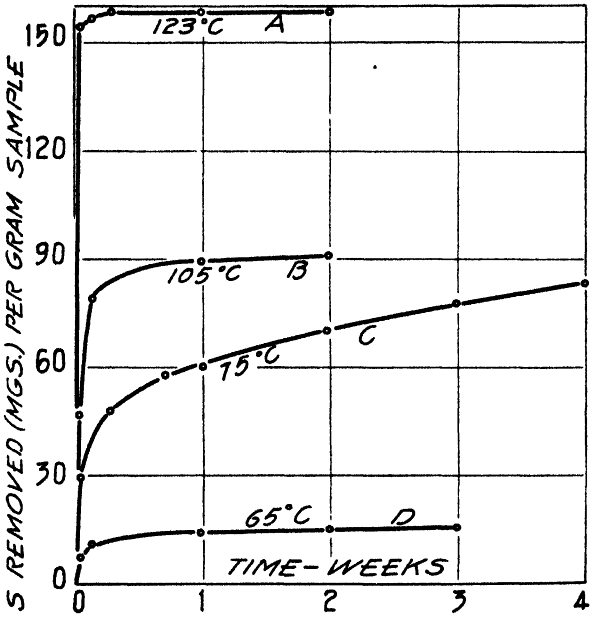


Fig. 7
Effect of continued heating on sulphur extracted from Pigment 7

Heating samples at 105° (Curve B) for 24 hours showed that the pentasulphide would furnish approximately one atom of sulphur as a separate phase, but further heating showed little effect. Temperature of 123° (Curve A) and above caused rapid decomposition of the pentasulphide, decomposition to the trisulphide being complete.

The results obtained here agreed in general with those obtained some twenty-odd years ago by Klenker[1]. Klenker found that 24 hours at 140°-150° gave complete decomposition to the trisulphide, while at temperatures above

---

[1] J. prakt. Chem. (2) 59, 193 (1899).

150°, oxidation of the sulphur and sulphide began to occur in noticeable amount.

From the work here described it may be concluded that pure pentasulphide will be more or less completely decomposed to the tetrasulphide if heated at temperatures 70-75°C. The tetrasulphide formed is slightly decomposed at 105° and rapidly so at 155-120°. These values for temperatures of decomposition are both slightly lower than those given by Klenker, and although requiring long periods of heating, are believed to be more correct.

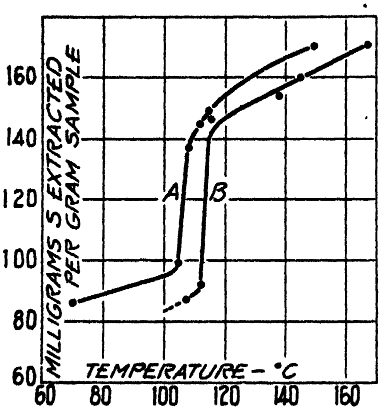


Fig. 8
Effect of Temperature on Pigment 3

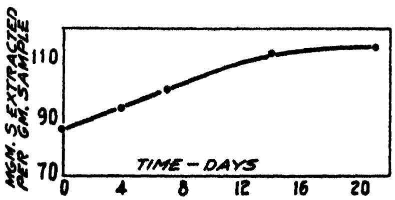


Fig. 9
Pigment 3 heated at 1050

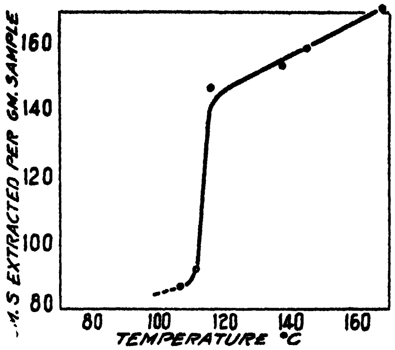


Fig. 10
Effect of Temperature on Pigment 3—168 hours

Similar study was given to the so-called antimony pentasulphide made by acidifying sodium thioantimonate. Pigments Golden 3 and Golden H were the samples used. Samples were heated at different temperatures, the time of heating being kept the same for each sample. The results of these tests are given in Tables VII-X, and are shown graphically in Figs. 8, 9, and 10.

Table VII. Effect of Temperature on Pigment H Heated 48 Hours. Fig. 8 Curve A.

y = milligrams sulphur extracted per gram sample

Temp.	y	Temp.	y
70°	86.0	112°	145.0
105	99.2	115	149.0
108	137.0	150	169.0

The last sample was heated but four hours.

TABLE VIII. Effect of Temperature on Pigment Golden 3. Heated 27 Hours FIG. 8. Curve B

y = milligrams sulphur extracted per gram sample

Temp.	y	Temp.	y
107°	87.0	138°	154.5
112	92.0	145	159.5
116	147.2	168	171.5

TABLE IX. Effect of Heat on Pigment Golden 3. Heated 168 Hours. FIG. 10.

y = milligrams sulphur extracted per gram sample

Temp.	y	Temp.	y
105°	99.2	135°	167.0
112	147.0	150	160.0*
120	164.0		

*Sulphur was subliming rapidly, and some was probably lost.

TABLE X. Effect of Heat on Pigment Golden 3 Heated at 105°C—varying time. FIG. 9.

Time in days

y = milligrams sulphur extracted per gram sulphur

Temp.	y	Temp.	v
0°	86.0	14°	111.0
4	93.6	21	113.0
7	99.2		

The work listed above on Pigments Golden 3 and Golden H agrees very well with that described by Klenker, and also with that done on the pure pentasulphide. The solid solutions of antimony tetrasulphide and sulphur are stable up to temperatures above 100°, the rate of decomposition being very slow at 105°–108°C.. At temperatures above 112–115° the decomposition of the material is quite rapid, and practically complete at 150°, even in a few hours.

The solid solutions evidently decompose rather easily, forming sulphur and antimony tetrasulphide as separate phases and this tetrasulphide decomposes at 115–120°C.

The main reactions that take place when antimony pentasulphides are heated are evidently as follows:

At temperatures up to approximately 110°

$$Sb_2S_5 \text{ (+ heat)} = Sb_2S_4 + S$$

From temperatures around 110° up to 150°

$$Sb_2S_4 \text{ (+ heat)} = Sb_2S_3 + S$$

Above 150°, the reaction is largely oxidation, or in the absence of air, subliming of the sulphur, with an accompanying change in the physical properties of the trisulphide formed.

The reactions for the pigments made from thioantimonates are similar to those of the tetrasulphide formed from the pentasulphides. The tetrasulphides are practically stable at temperatures up to approximately 110°. The change below those temperatures is very very slow.

In drying the residues after extracting sulphur from samples of pigment Golden 3, it was noted that some residues darkened in color much more rapidly than did others, and that this effect is most noticeable in the cases where the amount of sulphur removed is greatest. In order to check this point up, a whole series of samples was tested.

Samples of the pigment (Golden 3) were treated with varying amounts of the acetone-chloroform solvent, as in our standard procedure. The solvent was then filtered off, the residues washed with acetone, alcohol and water, and dried at 100°C. The dried residues were then placed in corked tubes, and subjected to a temperature of 130° in a hot air oven. They were observed at intervals, to note any sign of blackening, or subliming of sulphur onto the walls of the tube. These times, along with those at which blackening was complete, were noted, and are shown in Table XI.

TABLE XI. Effect of Heat on Pigment Golden 3 after Partial Extraction of Sulphur.

S Extracted Mgs.	Blackening started		Blackening completed	Sulphur separating
78.5	1st	18 hrs.	First	
75.6	2nd	24 hrs.	Second	36 hrs.
75	2nd	24 hrs.	Third	
55.2	3rd	36 hrs.	Fifth	
44.9	4th	36 hrs.	Sixth	
26.9	5th	144 hrs.	Seventh	96 hrs.
16.6*	4th	36 hrs.*	Fourth*	

*This sample is the only one out of order in the series. This exception is probably due to the fact that the tube was broken in handling, and the pigment recovered as well as possible. Impurities may have been introduced which accelerated the blackening.

The change in color of the pigment under these conditions is evidently a physical one only. The solid solution of antimony tetrasulphide and sulphur, and all the tetrasulphide itself is broken down, at this temperature in the first 24 hours, to trisulphide and more sulphur. The change in color is due to change in the physical condition of the trisulphide. This change in the color of the antimony trisulphide takes place rapidly at higher temperatures. (See this paper, page 229). The excess sulphur liberated in the decomposition of the tetrasulphide evidently decreases the velocity of the reaction. This effect may be due to some actual chemical effect of the excess sulphur, but it is much more likely that its effect is due to a purely physical effect, namely, separating the particles of the trisulphide by forming a thin layer between the particles. Its effect may also be due in part to the fact that the higher percentage of sulphur present may mask the first slight color change, and prevent the darkening from showing up at the time it would otherwise be noted.

Summary

(1) Antimony pentasulphide may be prepared by following carefully the directions given by Bunsen and Bosek. All the antimony must be carefully oxidized, the acidity adjusted, solutions kept cool, and the saturated hydrogen sulphide water added rapidly to excess. The working limits for the reaction are rather narrow.

(2) Pure antimony pentasulphide is not decomposed by cold sulphur solvents.

(3) Pure pentasulphide is decomposed by temperatures above 70°C., and quite rapidly by temperatures around 100°C. Hot sulphur solvents, especially carbon bisulphide, have some decomposing effect. Long heating breaks the pentasulphide down, liberating one atom of sulphur, and forming antimony tetrasulphide.

(4) Passing a slow stream of hydrogen sulphide through an antimonic acid solution reduces some of the antimony, forming antimony trisulphide and free sulphur.

(5) The decomposition of sodium thioantimonate with dilute acid does not form antimony pentasulphide, but a mixed pigment consisting of sulphur and a solid solution of sulphur in antimony tetrasulphide. The amount of solid solution present may be changed by changing the conditions of the decomposition reaction. The composition of the solid solution may be varied between that corresponding to $Sb_2S_{4.66}$ and Sb_2S_4.

(6) The solid solution of sulphur in antimony tetrasulphide is decomposed by heating at temperatures above 100°C. The tetrasulphide is rapidly decomposed into trisulphide and sulphur when heated above 115°C.

(7) The pigment formed by the interaction of trivalent antimony in acid solution and sodium thiosulphate does not contain antimony pentasulphide or antimony oxy-sulphide. The pigment is trisulphide and sulphur alone. There are no evidences of the formation of any solid solution.

(8) Removal of sulphur from the higher sulphides of antimony is a relatively simple matter, but the addition of sulphur, other than mechanically, has not been feasible.

(9) The presence of intimately mixed sulphur appears to have a retarding effect on the decomposition of antimony tetrasulphide by heat, and the subsequent change in physical properties of the trisulphide formed.

(10) A method is given for the study, from a phase rule point of view, of an irreversible equilibrium, enabling one to determine the composition of the material when a chemical analysis will not answer.

II. Colors of the Antimony Sulphides

The first part of this paper dealt with the nature and number of phases in so-called antimony pentasulphides. This latter half will be taken up with a study of the colors of antimony sulphides. The object of this study will be to account for the different colors found in the sulphides.

Antimony trisulphides may be prepared which vary in color over a wide range. The tetra- and pentasulphides of antimony do not show such a variety of colors. The trisulphides will be taken up first.

Antimony trisulphides have long been divided into two classes—the natural variety, and the artificially prepared varieties. In general, the latter class includes all the colored trisulphides.

The natural variety of antimony trisulphide is the mineral stibnite. It is the most important source of antimony. Stibnite is crystalline—either hexagonal[1] or rhombic[2]. It is variously described as black, (steel-gray, gray, etc.) brittle needles which melt at about 550°C. Dana[3] states that it possesses a metallic luster. Stibnite is a poor conductor of electricity. On exposure to light it shows a voltage effect like that shown by some selenium compounds.

In addition to the well-known stibnite, there also exists a natural brick-red antimony trisulphide, said to be amorphous[4]. This is known as meta-stibnite. It will not be considered here.

The artificial trisulphides vary widely in color and other properties, depending on methods of preparation. From any of these artificial trisulphides, a black crystalline trisulphide may be prepared. This latter variety is very similar to stibnite: later in this paper, it will be shown that the two are identical. (See page 237)

The other artificial trisulphides may be prepared, varying in color from a very light yellow, through a series of shades of orange, red, maroon, and brown to black. The red and maroon shades can not be prepared in the ordinary way. The presence of hydrogen sulphide in the solutions from which the sulphide is precipitated is found to prevent the formation of these shades.

Williams[5] has recommended that the artificial trisulphides be divided into two sub-groups. The first group should include all those sulphides of antimony precipitated in the presence of hydrogen sulphide. This includes all the sulphides precipitated by hydrogen sulphide direct, those formed by the interaction of acids with thioantimonites or thioantimonates, and those precipitated by treating stibnite with sulphur in sunlight. This group may be called the "antimony goldens".

The second group of artificial trisulphides should include those formed in the absence of hydrogen sulphide. This is the group that gives us our greatest variety of colors. Although much lighter sulphides may be formed, those formed by these methods at moderate temperatures are usually some shade of red. This group may be called the "antimony crimsons."

Williams[6] showed that the color of the precipitate obtained was, in general, darkened by increasing the temperature, acidity, or the length of time of the reaction. All these factors may cause the formation of larger particles or agglomerates. This makes it appear likely that a large part, if not all, of the difference in the colors of antimony trisulphides may be explained or accounted for simply by this change in particle size. A series of experiments was run to test out this point.

The addition of any substance which would tend to cause the formation of a larger particle would be expected, according to this idea, to form a darker colored pigment. Antimony sulphides as sols are stated to be negatively charged[1]. The addition of an acid or a salt giving an easily adsorbed positive ion that should tend to coagulate sulphides more readily. On the other hand, the addition of a substance furnishing a readily adsorbed anion, or furnishing a colloid which may be readily adsorbed and so act as a protecting colloid, would give more finely divided particles, which would be expected to be of a lighter color. Higher temperature of reaction will also tend to agglomerate the particles.

---

[1] Olsen: "Chemical Annual", pp. 184-5 (1922).

[2] Moissan: "Traité de Chimie minerale", 2, 42 (1905).

[3] Dana: "A System of Mineralogy", p. 36.

[4] Becker: Am. Phil. Soc., 25, 168 (1888).

[5] Unpublished report—privately communicated.

[6] Unpublished report—privately communicated.

The golden trisulphides offer a rather limited range of colors, so the crimson sulphides were chosen at the first series of tests.

Crimsons were made for this first series by precipitation of the sulphides from a solution of potassium antimonyl tartrate mixed with sodium thiosulphate. The strengths of these solutions were fixed at twenty grams of antimony per liter of the tartrate solution, and five hundred grams of the anhydrous sodium thiosulphate per liter of solution. The gelatin contained fifty grams of gelatin per liter.

Five cc samples of the tartrate solution (equivalent to 100 mg. of antimony) were placed in test tubes. The desired amount of gelatin was then added to each tube, and the total volume brought up to ten cc, using distilled water. Five cc of the thiosulphate solution were then added to each tube, all the tubes stoppered, heated to the desired temperatures, and the results observed.

The results of these tests were striking. At room temperature, samples to which little or no gelatin had been added gave a light red suspension, which settled slowly. After two days these suspensions had settled out as red precipitates, giving clear, water-white supernatant liquids, which were found to be free from antimony. This indicated that the precipitation of the antimony was complete.

The addition of as much as one milligram of gelatin showed an appreciable effect. Further additions of gelatin showed three effects: (1) the colors of the suspensions and precipitates became lighter in color; (2) the amounts of precipitates were decreased, and the removal of the antimony incomplete; and (3) the liquid became more cloudy. When the point was reached at which about six milligrams of the gelatin had been added to the samples, the suspensions became much more clear; when as much as twelve milligrams of the gelatin had been added, the entire suspension was perfectly clear, brightly golden in color. The amounts of precipitates had become practically zero. Even after standing three months, the pigments were still in colloidal suspension.

The addition of larger amounts of gelatin showed little or no effects on the colors of the suspensions or precipitates. At very high concentrations of the gelatin, the thiosulphate solution caused some of the gelatin to coagulate, again giving a cloudy suspension.

At higher temperatures the effects of the gelatin were similar to those at room temperature, but much more pronounced. The colors of the samples were in every case darker than in the corresponding samples of the series at room temperature. The amounts of precipitate were increased.

---

[1] Picton: J. Chem. Soc., 61, 116 (1892).

The addition of acid to sample tubes gave the results expected. Very dilute hydrochloric acid solutions were used. These caused more immediate and complete precipitation of a darker colored sulphide, than the corresponding sample in the neutral series.

The addition of the alkali had an opposite effect, lightening the colors of the precipitated sulphides, and decreasing the amounts of precipitates. The upper limit for the addition of alkali was reached when the antimony began to precipitate as the hydroxide or a basic salt.

Using a slit ultramicroscope (Zsigmondy) the sizes of the particles from different samples, prepared as above, were measured. The particle sizes ranged from 0.25-0.4μ up to much larger sizes. The larger sizes had agglomerated so badly that a correct estimate of particle size was impossible. Counting the number of particles per field of the ultramicroscope, showed that the colors of the samples steadily darkened as the particle size increased. Series of samples arranged in colors grading from light to darker shades were found to contain particles of regularly increasing size. This agreed exactly with the results predicted.

From the preceding experiments it was thought likely that the colors of samples of antimony trisulphide might be appreciably lightened by grinding or in any other way reducing the particle sizes[1]. Unfortunately, grinding artificial antimony sulphides causes the formation of the black variety[2]; this effect is probably due to the heat developed by the grinding. The effect of heat on the dry powder was taken up in a later part of the study. It is sufficient here to state that the effect of heat developed in grinding the dry trisulphide in a mortar is more than sufficient to off-set any change in color due to reduction in particle size.

Grinding under water was then attempted, with little noticeable results. In order to prevent agglomeration of particles which might be reduced to very small sizes, some gelatin was added to the water.

A fresh sample of stibnite was ground to a fine powder. A dilute gelatin sol was added to the mortar and the mixture well stirred. It was then divided into equal parts, one part poured into a test tube. The other half was left in the mortar, and the mixture thoroughly ground with the pestle. After long grinding the mixture from the mortar was poured into a second tube and allowed to set to a jelly. The first sample had set solidly, the heavier particles going to the bottom of the tube and concentrating before the gelatin had begun to set. The upper portions of the tube showed lower concentrations of black particles, while an almost clear layer of jelly was formed at the top. The second sample, which had been ground in the presence of the gelatin, showed similar effects. In this latter case, however, the top layer of the gel, although clear, showed traces of a reddish color. This effect was so slight that the experiment was repeated—with the same results.

---

[1] Bancroft: "Applied Colloid Chemistry", 148, 205 (1921).

[2] Von Bacho: Ann. chim. applicata, **12**, 143-152 (1919).

This experiment showed that reduction of particle size of the stibnite, known to be crystalline, tended to change the color from gray-black to reddish. The experiment was encouraging but not conclusive.

Bredig[1] and Svedberg[2] have prepared colloidal solutions of practically all the metals. They made use of electrical dispersion methods. It was thought worthwhile to attempt the preparation of finely divided sulphide by electrically dispersing stibnite. This method should, it was thought, give a lighter colored—(at least a colored)—sulphide.

A set-up was arranged by means of which a high voltage arc could be formed between stibnite electrodes immersed in cold distilled water[2]. With 4,000 volts the reaction was almost explosive. Some of the electrodes was disintegrated and settled to the bottom of the cell, as a bright yellow sludge. As the time for the current increased the temperature of the water increased rapidly, and the color of the sludge became darker. When the temperature of the water had reached approximately 75°C., the formation of the yellow particles ceased.

The colored substance formed by this electrical disintegration was analyzed and proved to be antimony trisulphide. The filtrate after removal of this trisulphide showed the presence of sulphate and sulphite ions. These substances were due, no doubt, to oxidation of a small part of the stibnite to antimony sulphate, or oxide. When sufficient electrolyte was formed, the solution carried most of the current and no stibnite was arced.

Experiments were made using higher and lower voltages, with inductance in circuit, and condensers in series or shunt with the cell. The differences in effects were not very marked. In general, the higher voltages gave more finely divided particles, while the use of a condenser apparently gave slightly coarser particles. The changes due to the differences in the electrical circuits, were more than off-set by the differences caused by the rise in temperature of the cell.

The effect of temperature of the cell was in every case in agreement with the effect on precipitated sulphides. Rising temperatures increased the particle size and darkened the color of the precipitate or disintegrated sulphide. The additions of small amounts of gelatin to the distilled water in the cell gave exactly the effects expected,—namely, a more finely divided and lighter colored sulphide. If sufficient gelatin were added, a suspension of the yellow trisulphide could be formed. This suspension was stable after three months standing. Here again, the gelatin acts as a protecting colloid, preventing the agglomeration of the finely divided particles, and so forming a clear colloidal suspension. The gelatin in this way tends to counterbalance the effect of the rising temperature.

[1] Z. Elecktrochem., **4**, 514 (1898); Z. physik. Chem., **31**, 258 (1899).

[2] "Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe", 424 (1909).

Having succeeded in preparing very finely divided trisulphides and shown that these were generally lighter in color, it was next thought possible to form large particles or crystals which would be of a darker color.

Methods were employed which are known to favor slow reactions and give opportunity for the growth of large crystals. Interaction of very dilute solutions, slow diffusion of solutions through diaphragms, and formation of the precipitates in gels, were all tried. Particular efforts were made to grow large crystals by diffusion through gels. Silica gel, gelatin, and agar agar were used[1].

The results agreed very well with each other but were not those hoped for or expected. Silica gels were made as directed by Holmes. When solutions of sodium thioantimonate were poured in on top of these gels and allowed to diffuse down, orange and brownish antimony sulphides were formed. The colors appeared little different from those of sulphides precipitated in the usual way,—except for one noticeable effect. All tubes showed pronounced Liesegang rings or rhythmic banding effects. These were particularly clear in cases where the surface of the gel was first washed with a solution of sodium carbonate, and a small amount of carbonate added to the thioantimonate solution. The carbonate prevented the rapid reaction at the surface of the gel.

Other samples of gel were prepared and antimony sulphides precipitated. The following methods of precipitation were used.

Gel Solution added.

(1) Silica gel (Acid) and sodium thioantimonate.

(2) Sodium thiosulphate in gelatin gel and $SbCl_3$ solution.

(3) Antimony chloride in gelatin gel and sodium thiosulphate.

(4) Same as (2) and (3) using agar agar in place of gelatin.

(5) Using a gel in the bottom of a U-tube, allowing the two solutions in the two arms of the tube to diffuse together.

Antimony sulphides were precipitated in every case. In most cases the rhythmic banding was noticeable. In no case was there any evidence of any noticeable increase in particle size. In cases wherever possible, the gel containing the sulphides was removed and the size of sulphide particles measured with the ultramicroscope.

In general, the size of antimony sulphide particles precipitated in gels by above methods does not differ from those precipitated in the usual manner. This matter was not carried further along these lines.

The experiments described above make the following conclusions obvious:

(1) Particle size is an important factor in affecting the colors of antimony trisulphides.

(2) Precipitated antimony trisulphides may tend to remain in suspension as negatively charged particles.

(3) Addition of acid tends to flocculate suspended trisulphide. Addition of alkali tends to peptize it.

---

[1] Cf. Holmes: "Laboratory Manual of Colloid Chemistry", 91 (1922).

(4) Heating suspensions tends to flocculate the sulphide and, if already precipitated, tends to darken the color of the precipitate.

(5) Addition of gelatin furnishes a colloid which is apparently easily adsorbed. This prevents agglomeration and causes the formation of a more finely divided pigment.

(6) Increasing temperature of reaction, addition of acids will give sulphides with a darker color.

(7) Addition of gelatin or alkalies to solutions, or mechanical reduction of particle size, tend to form lighter colored sulphides.

(8) Using a method similar to that described by Svedberg, natural black antimony trisulphide may be electrically disintegrated, giving a finely divided sulphide which is similar to the ordinary precipitated antimony sulphide.

(9) The methods used to grow large crystals of antimony sulphide were not successful. Precipitation of the sulphides in gels showed Liesegang ring effects.

The effect of increasing temperature on the colors of suspensions or precipitates of antimony trisulphides has already been discussed, p. 222. The effect of heat on dry antimony sulphides was also studied. It was found that in this case, too, heating dry antimony trisulphides caused noticeable changes in color. Continued heating at relatively high temperatures caused all the antimony sulphides to become entirely black. The object of this study was to account for these color changes.

These changes in color have already been the subjects of considerable study[1]. Von Bacho[2] made a careful study of the effect of heat on the color changes of the sulphides of antimony. His work dealt, for the most part, with the change to the black modification, and the effect of impurities on the rate of this change. Von Bacho concluded that the black modification contains "traces of colloidal antimony, in consequence of an almost imperceptible decomposition due to chemical or mechanical causes." This conclusion can not be checked easily. The effects of impurities as listed by von Bacho have, in most cases, been checked by Williams. The presence of salts, particularly the chlorides, and of acids, was found to lower the temperature at which the change to the black modification was complete. Sodium chloride, antimony oxy-chloride (or chloride) and hydrochloric acid were found to be very sufficient in promoting the change to the black crystalline form. Hautefeuille and Perrey[3] found that under certain conditions hydrochloric acid gas causes amorphous oxides of aluminum, titanium, and zirconium to change to the corresponding crystalline oxides.

Von Zani[4] also states that one cause for the formation of the black trisulphide is the coating over of the individual particles with a film of metallic antimony. The formation of the metallic antimony is said to take place as follows: the amorphous trisulphide readily absorbs oxygen, then loses sulphur dioxide, leaving small particles of metallic antimony. This theory could not be checked analytically. Furthermore, the colored trisulphides change to the black modification quite readily when heated in the absence of oxygen. Heating the sulphides in an atmosphere of hydrogen sulphide gives a rapid change[1], while heating in carbon dioxide or in sulphur dioxide also gives the black modification.

---

[1] Gmelin-Kraut: "Handbuch anorg. Chem.", 311, 699-705; Guinchant and Chrétien: Compt. rend., **138**, 1269 (1904); **139**, 51, 288 (1904); **142**, 709 (1906).

[2] Ann. chim. applicata, **12**, 143 (1909).

[3] Compt. rend., **110**, 1028 (1890).

[4] Chem. Abs., **4**, 2758 (1908).

It is a well-known fact that the degree of fineness of powdered materials may have a decided effect on their colors. Red mercuric oxide may be ground to such a fine powder that the color is no longer red, but yellow. Potassium ferricyanide is brown-red in coarse crystals, and yellow when powdered. Ferric oxide has been prepared in both red and yellow forms, the yellow being the finer powder. Thin plates of hematite are yellow by transmitted light, the color varying with increased thickness through reddish brown to deep brown red or blood red[2]. The massive hematite may be almost black, although its streak is always reddish. Size of particle also has an important bearing on the colors of antimony sulphides. This will be shown below.

To explain the color changes observed when dry antimony trisulphide is heated, the following hypotheses are made: (1) Antimony trisulphide exists in both the crystalline and the amorphous states. (2) Very finely divided crystalline trisulphide is yellow, while the slightly larger crystals are black. (3) Finely divided amorphous trisulphide is also yellow; coarser amorphous antimony trisulphide is crimson. (4) The black crystalline modification is the stable one at high temperatures.

An effort is here made to justify these assumptions and with them to explain the color changes of the antimony trisulphides.

By means of X-ray diffraction patterns, the existence of both amorphous and crystalline states of antimony trisulphide may be proved. (This work is described on pages 236-237 of this paper.) This method gives definite proof of the existence or non-existence of a crystal structure in a material. Antimony trisulphides may be prepared in either the amorphous or the crystalline form.

It has already been shown that black crystalline stibnite may be electrically disintegrated to give a yellow trisulphide. (Page 227.) Ultramicroscopic measurements show that the yellow particles are very finely divided—much more so than could be accomplished by mechanical methods of size reduction. Chemically, the yellow sulphide is identical with the original stibnite. By X-ray methods the crystal structures of the two are shown to be identical. It is therefore considered that the reduction in particle size is the only cause of the difference in color between the yellow and the black crystalline forms.

The interaction of solutions of sodium thiosulphate and antimony chloride will, at room temperatures, give a light yellow precipitate. This may be filtered off, washed thoroughly and dried in a vacuum desiccator over sulphuric acid. The resulting product is a fine yellow powder, which may be easily passed through a 100-mesh sieve, no crushing or grinding being required. If this fine powder is placed in an air oven at 105°-110°C., a marked difference in color will soon appear. The color will change steadily, passing through orange shades, finally reaching a point at which all of the yellow color will have disappeared and the powder is uniformly red. Further heating at this temperature forms a rich crimson colored powder. If the oven temperature is next raised to 150-170°C., and the heating continued at this temperature, the color of the sulphide changes slowly, passing through a series of shades of crimson and maroon[1], finally becoming uniformly black.

---

[1] Mourlot: Compt. rend., **123**, 54 (1896); Ann. Chim. Phys., **7**, 17 (1899).

[2] Bancroft: "Applied Colloid Chemistry", 205 (1921).

Measurements with the ultramicroscope show that the yellow sulphide is more finely divided than the various orange shades, while the latter are finer than the crimson particles. The increase in particle size follows in the same order as the changes from yellow through to red and crimson. Beyond the crimson stage, the change (if any) is too slight to be measured.

Both the yellow and crimson sulphides as prepared above may be proved amorphous. The final black form is crystalline, (see pages 237).

The precipitation of the trisulphides of antimony, as described above, may be varied within limits and the resulting sulphides will tend to vary in color, depending on the exact conditions. In every case, it will be found that the same set of conditions that tends to give a more finely divided precipitate will always give an antimony sulphide with a lighter yellow color, (see page 225).

These experiments show that our assumption, of a fine yellow and a coarser crimson amorphous antimony trisulphide, was justified.

The tendency of all antimony sulphides to change at high temperatures to the black crystalline trisulphide has long been recognized. The temperature at which the change to the black form begins, and that at which the change is complete, varies with the purity of the sulphide and the method used in preparing it[2].

The maroon shades may be considered as mixtures of red with a certain amount of black. The maroon shades of antimony sulphides are very little, if any, larger than the crimson material. The formation of the various maroon shades is considered as resulting from the formation of increasing amounts of the black modification of the trisulphide. This black material when mixed in with the crimson powder, gives the maroon shades. Under the microscope the maroon sulphides appear homogeneous, so it is evident that the black modification forms in small amounts in the crimson particles themselves. What probably happens is that some of the crimson particles in a particular aggregation change to the black, but being so small, the black particles can not be distinguished from the red particles around them. The same shades of maroon pigment may be duplicated by mixing the correct proportions of the crimson and black modifications. Here, however, the two phases may be distinguished under the microscope.

---

[1] The names "crimson" and "maroon" as here given to the colors of the antimony sulphides, are the names used in the industry manufacturing these sulphides for use as pigments.

Webster's New International Dictionary defines these words as "maroon—sometimes a dark brown chestnut color; ordinarily, any red of dull luminosity, a dull red". "Crimson—a deep red color tinged with blue, one of the primary pigment colors; also red color in general".

The pigment color here called crimson is a rich red, but does not appear to contain any blue tinge. The maroon color does not appear to contain any brown color. Both the crimson and the maroon are dark reds, the maroon shades appearing much darker. They are later shown to be mixtures of the crimson and black.

[2] Abegg: "Handbuch anorg. Chem.", 3 III, 598 (1907); Moissan: "Traité de Chimie minerale, 2, 10, 47 (1905); Unger: J. Chem. Soc., 25, 41 (1872).

Further corroboration, of the statements made above, may be found in the fact that the densities of the sulphides are found to change in exactly the same order as do the colors: the yellow pigments have a density of approximately 4.10-4.12, the crimson 4.12-4.38, while the black form has a density[1] of 4.6-4.8. The density of the maroon shades is usually about 4.4-4.5: the approximate density may be calculated if the color of the pigment is matched with a mixture of known amounts of crimson and black sulphides of known densities.

It may thus be seen that the existence of yellow and crimson amorphous trisulphide and a black crystalline modification will explain the color changes observed when a certain antimony sulphide is heated. The formation of the maroon-colored sulphides offers no particular difficulty. The finely divided crystalline yellow sulphide is not ordinarily formed and does not occur in most sulphides.

There yet remains one class of antimony trisulphides that requires some consideration and explanation.

Williams has noted that no crimson-colored pigment is formed if the sulphide is precipitated in the presence of hydrogen sulphide. Antimony sulphides as ordinarily precipitated by hydrogen sulphide from solutions of trivalent antimony, at room temperature are light golden yellow. On standing at room temperature, the precipitate settles slowly and darkens slightly. If it is next filtered off, washed thoroughly, and dried over sulphuric acid in a vacuum desiccator, the resulting pigment will be a rich golden. Heating this golden pigment at 105°-110°C. causes little or no color change, except perhaps, a slight dulling of the color. Further heating at higher temperatures (150°-170°C.) causes the pigment to change through varying shades of brown to the black modification.

The brown pigments are considered mixtures of varying proportions of yellow (golden) and black trisulphides. The brown colors may be duplicated by mixing the proper proportions of black trisulphide with the golden pigment. As in the case of the maroon shades, the densities of the brown pigments lie between the densities of the light colored and the black modifications. Under the microscope, both brown and maroon pigments made by mixing black with the colored pigments may be distinguished as mixtures. The corresponding colors made by heating the golden and crimson sulphides do not appear as mixtures, but are quite homogeneous to the limit of magnification. This shows that the formation of the black modification takes place very uniformly throughout the pigment, and forms in very small particles or crystals.

---

[1] Kirschoff: Z. anorg. Chem. **114**, 266 (1920); Guinchant and Chrétien: Compt. rend., **138**, 1269 (1904); **139**, 51, 288 (1904); **142**, 709 (1906); Fehling: "Neues Handwörterbuch Chem." **1**, 698 (1874); Roscoe and Schorlemmer: "Treatise on Chemistry", 970 (1895).

None of the above offers any explanation of the fact that golden sulphides, precipitated in the presence of hydrogen sulphide, will not darken through the crimson stage.

It is supposed that some factor prevents the growth of the particles of the amorphous golden to the size of the crimson particles. Before the conditions required to form the crimson are reached the golden begins to change to the black modification, and we have the series of shades of brown to black, instead of the crimson and maroon shades.

The formation of a protecting film around each particle of golden pigment would prevent intimate contact and the formation of the crimson particles. The color of the powder would, under these conditions, tend to remain the same as that of the individual particles which are originally yellow or golden. If this film could be removed agglomeration would take place unretarded, forming first the crimson pigment, then the maroon shades, and finally the black form.

It is not difficult to prove that such a film may cause the effect observed in the case of antimony goldens. If a sample of the dry pigment prepared from sodium thiosulphate and antimony trichloride, as above, dried over sulphuric acid is moistened, with a gelatin sol, the color changes on subsequent heating at 105°C. will be much like those observed for golden antimony. The effect is further increased if some gelatin sol is present in the solution when the sulphide is precipitated.

The effects always caused by hydrogen sulphide lead one to believe that it is this substance that forms the film over the particles of antimony sulphide. This idea was checked up in the following experiments.

The addition of a very small amount of sodium sulphide to the sodium thiosulphate solution used in precipitating sulphides of antimony will tend to give a precipitate that is much lighter in color than that formed in the absence of the sodium sulphide. When this precipitate is filtered off, washed dried and heated as above it behaves like the antimony goldens and not like the crimson sulphides, as might be expected. In other words, its color changes are like those of sulphides entirely precipitated by hydrogen sulphide. As little as one-half of one percent of sodium sulphide will cause this effect.

In order to prepare a sulphide of antimony in the absence of hydrogen sulphide, excess salts or acids, an electrolytic method was decided upon. (Compare LeBlanc and Schick: Z. physik. Chem., **46**, 213 (1903) White: Trans. Am. Electrochem. Soc., **9**, 305 (1906).)

In order to carry out this method an electrolytic cell was arranged using electrodes of pure antimony metal. These were immersed in a solution of sodium thiosulphate and a current passed through. Different strengths of solution and varying currents were used. Alternating current electrolysis was tried, and found to give fair results. Due, however, to a tendency of the sulphide formed to stick to the electrodes necessitating continual scraping, it was decided that for most of this work direct current would be preferable.

In a cold solution of concentrated thiosulphide the passage of the current carried antimony into solution as ions. These immediately reacted with the thiosulphate ions present, and then decomposed to form antimony trisulphide, which precipitated. This precipitate was light yellow in color. At higher temperatures, the formation of the precipitate was much more rapid, and the color of the sulphide slightly more golden in color.

This electrolytic pigment was filtered, washed and dried. On heating the colors did not pass through the maroon and crimson stages, but were found to change through the brown and black. This was hardly as expected, so an explanation was sought. It was easily found when it was observed that at the cathode of the cell, some stibine and some hydrogen sulphide was liberated. This, of course, was equivalent to precipitating the sulphide from thiosulphate solution in the presence of hydrogen sulphide, and this has already been described as giving the golden modification. This difficulty was easily eliminated by using a porous diaphragm around the cathode, and thus keeping the hydrogen sulphide solution from mixing with the solution containing the thiosulphate and precipitated sulphide. The precipitate as formed in the anode compartment was then found to act exactly as the samples of crimson prepared in the usual way.

As would be expected from the first part of this work (see page 229) the formation of electrolytic antimony sulphides in more concentrated solutions at low temperatures, or with the addition of a small amount of gelatin sol, was found to give a precipitate of smaller particle size, and of a lighter color.

The following method was suggested to definitely establish the fact that golden antimony sulphides actually contain hydrogen sulphide, probably as an adsorbed film. A sample of pure trisulphide was washed, dried, extracted with carbon tetrachloride, and then thoroughly dried at 105°C. for two months. The resulting trisulphide was a light golden color. Samples of this pigment were then placed in small glass tubes of thick-walled Pyrex glass, evacuated to a pressure of less than one millimeter, and sealed off. The tubes were then placed in an electric furnace and heated at temperatures of 200-225°C for six hours. They were then removed and slowly cooled.

The pigment in the tubes was all converted to the black crystalline variety—as was expected. When the tubes were scratched and broken, a pronounced odor of hydrogen sulphide was noticed.

Adsorption of the hydrogen sulphide by the antimony sulphide is a surface effect. Any hydrogen sulphide not adsorbed would be removed by the treatment given the pigment before sealing in the tubes. Heating the pigment at the high temperature caused the adsorbed gas to be driven off into the evacuated tube. When the pigment crystallized, with much larger particles, and hence much less surface, the gas was not re-adsorbed on cooling.

Antimony crimson samples, similarly treated, gave no indication of liberated hydrogen sulphide. This seemed to prove definitely that hydrogen sulphide is adsorbed by the antimony sulphide whenever the gas is brought into contact with the pigment. This was proved in a similar manner, by exposing crimson antimony to hydrogen sulphide, again washing, drying, extracting and drying, evacuating and sealing the tube. When this tube was heated, cooled and broken, a trace of hydrogen sulphide was noted, although much less than in the case of the golden where the gas was adsorbed at the time of precipitating.

The preceding experiments definitely prove that antimony sulphides precipitated in the presence of hydrogen sulphide constitute an entirely different class from those precipitated in the absence of this substance. The essential difference between these two classes lies in the color changes resulting when the two kinds are heated. One class may form a brown material, the second class under the same conditions giving a maroon material. The cause for this difference is the formation of an adsorbed film of hydrogen sulphide on particles of antimony sulphide precipitated in the presence of this compound.

In carrying out several of the preceding experiments, it was noticed that antimony sulphides often tended to show pretty series of film colors. Several tests were made to form these films.

It was found that coating a glass plate with a dilute solution of an antimony salt, allowing the solution to evaporate almost completely, and then exposing to hydrogen sulphide fumes formed a thin film of the antimony trisulphide which showed many of the effects of Newton's rings[1]. On carefully heating the center of the glass plate, the sulphide in the center will change to orange and then to black, leaving more or less concentric rings of vari-colored sulphides.

If graphite electrodes are placed in a suspension containing very finely divided antimony sulphides, and a low voltage applied, the electrodes will be coated with a thin film of the sulphide. This film may vary in color, depending on thickness, etc.; but in general will show blue, green and yellow.

The same-colored film effect may be secured by subjecting electrodes of stibnite held a few centimeters apart in an evacuated system, to very high voltages. The cathode becomes coated with the colored film, probably metallic antimony, for a trace of sulphur may be driven out of the stibnite.

These film colors of the sulphides are striking and quite interesting but they should not in any way be confused with the actual pigment colors.

The effect of heat on the colors of the antimony penta- and tetrasulphides was mentioned on page 222 of this paper. In general, the effect of color is but slight, a general darkening being the most noticeable effect. After the decomposition to the trisulphide is complete, the color changes are then like those of all the trisulphides precipitated in the presence of hydrogen sulphide. Heating at moderate temperatures (150°C.) may cause appreciable darkening of the higher sulphides before all the higher sulphide is decomposed to the trisulphide. This darkening may be explained as the result of the formation of black trisulphide throughout the mass of pigment, causing any unchanged higher sulphide or trisulphide to appear brown.

---

[1] Tyndall: "Electricity and Light", 97 (1895)

It was considered worth-while to make a study of the crystal structure of the different antimony sulphides. For this work, X-ray powder photographs of the sulphides were made. The apparatus used was that described by Davey[1]; a complete description of this apparatus will be omitted here. It is based on the principles discovered and worked out by Laue[2] and the Braggs[3] and later modified by Hull[4].

The samples of sulphides to be studied were finely powdered, placed in thin-walled glass tubes of about 1/32 inch inside diameter, and placed in position in the apparatus. A monochromatic beam of X-rays (the Molybdenum K-alpha doublet) reduced to a suitable slit system (see Davey page 566) was then passed through the sample tube. The X-ray diffraction pattern was recorded on a strip of photographic film placed in a cassette which automatically held the film on the arc of a circle of 8-inch radius, having at its center the sample of powdered sulphide.

The photographs of X-ray diffraction patterns look very much like the pictures of line spectra. A full account of the mathematical theory of the pattern is given by Hull.

For this work on antimony sulphides the following samples were prepared and their X-ray diffraction patterns taken:

(1) Metallic antimony.
(2) Sulphur, both precipitated and "flowers."
(3) Antimony pentasulphide.
(4) Antimony tetrasulphide.
(5) Antimony trisulphides:
    (a) Precipitated golden trisulphide.
    (b) Precipitated crimson trisulphide.
    (c) Electrolytic trisulphide (see page 233 of this paper).
    (d) Natural stibnite.
    (e) Stibnite disintegrated by the Svedberg arc.
    (f) Artificial black trisulphides.

Patterns of these samples were taken separately, or simultaneously with that of NaCl, in order to give a comparison scale. The time required for exposure in order to give clear patterns varied with the nature of the samples. NaCl gave a clear pattern in five hours. For the other samples, approximately twenty hours was found to be the most satisfactory length of exposure.

It was hoped that this method would show different crystal structures for the tri-, tetra-, and pentasulphides of antimony, and so furnish a convenient method of distinguishing between them. The results of these efforts were rather surprising. Instead of giving different patterns for each sulphide, all of the precipitated sulphides of antimony were alike in that none gave X-ray diffraction patterns or any indications of definite crystal structure. They are evidently amorphous substances[1].

---

[1] Gen. Elec. Rev., **25**, 565 (1922).

[2] Sitzungsber. bayr. Akad. Wiss., (1912).

[3] W. H. and W. L. Bragg: "X-rays and Crystal Structure", (1915).

[4] Phys. Rev., **10**, 661 (1917); Proc. Am. Inst. Elec. Eng., **38**, 1171 (1919).

This conclusion was at first doubted, but further work on the subject leaves little doubt that the precipitated sulphides of antimony—including the tri-, tetra-, and pentasulphides are really amorphous precipitates. All efforts to obtain patterns showing a crystalline formation have failed. Prof. Debye and Dr. Davey both agree that the indications are very strong that we have truly amorphous substances.

The cases of sulphur and antimony were much more simple. Both gave the diffraction patterns expected[2].

Precipitated golden and crimson trisulphides, and the "electrolytic trisulphide" are evidently amorphous.

The natural stibnite, artificial black trisulphides, and the trisulphide disintegrated by the Svedberg arc, all are crystalline and show the same diffraction pattern. This is particularly interesting if one remembers that the disintegrated material is golden in color, and very similar to the precipitated amorphous material. This is the only case in which a colored antimony sulphide was found to have a definite crystal structure. The method of preparation of the artificial black trisulphides seemed to have no effect on the crystal structure of the resulting product.

Conclusions

(1) Precipitated antimony sulphides are all amorphous solids. These include antimony pentasulphide, antimony tetrasulphide, and both golden and crimson antimony trisulphides. All these sulphides are colored.

(2) All amorphous sulphides of antimony may be converted into the black crystalline modification of the trisulphide by long heating at high temperatures—around 200°C. The resulting black modification is the same regardless of the sulphide used as the starting material.

(3) The amorphous antimony trisulphide in a very fine state of subdivision is yellow. Larger amorphous particles are crimson in color. Intermediate colors are also of intermediate size or mixtures of the yellow and crimson.

(4) Maroon shades of antimony trisulphide are mixtures of crimson and black sulphides.

(5) A crystalline yellow antimony trisulphide may be prepared by means of electrical disintegration of stibnite under water. This colored crystalline material shows exactly the same crystal structure as do all the artificially prepared crystalline sulphides of antimony. The yellow crystalline form is the very finely divided crystalline form. All the artificially prepared crystalline sulphides of antimony show a crystal structure identical with that of stibnite, the natural crystalline variety.

---

[1] Haber: Ber. 55B, 1717-1733 (1922)

[2] Wyckoff: "The Structure of Crystals" (1924).

(6) Antimony pigments precipitated in the presence of S″ or HS′ ions will not darken through crimson and maroon shades, but instead darken through varying shades of golden to brown and then to the black modification. The difference between the brown and the maroon pigments is due to the adsorption of a film of hydrogen sulphide by the former. This adsorbed film prevents the intimate contact of the particles, and so prevents the growth of larger particles forming the crimson variety. The varying shades of brown may be explained as resulting from mixing the golden pigment with varying quantities of the black modification.

(7) Crystalline crimson pigment can not be prepared by any of the methods studied. The golden variety may be prepared amorphous by precipitation, crystalline by disintegration of stibnite. The larger particles of amorphous trisulphide alone give the crimson variety.

I welcome this opportunity to acknowledge my indebtedness to Professoı Wilder D. Bancroft, and to express my gratitude to him for the many helpful suggestions and valuable criticisms offered during the progress of this work.

I also wish to express my thanks to Professor F. K. Richtmyer and Mr. H. W. Russell for their co-operation and suggestions in carrying out parts of this work.

Cornell University

THE APPARENT VISCOSITY OF COLLOIDAL SOLUTIONS AND A THEORY OF NEUTRAL COLLOIDS AS SOLVATED MICELLES CAPABLE OF AGGREGATION*

BY JAMES WILLIAM MCBAIN

Our work on nitro cotton led several years ago to a hypothesis which has proved useful throughout subsequent experiment. It attempts to explain viscosity relationships and their changes with time and conditions, the structure of jellies and their reversible changes; and it emphasizes the relation between solvent and colloid ascribing to solvation a role which we believe to be of far more general importance than the more familiar electrical charges.

A. *The mechanical explanation of viscosity.*

There are four ways of explaining the high viscosity of colloidal solutions, suspensions and emulsions as compared with the viscosity of the solvent:—

a) The increased shear imposed upon the solvent for a given amount of flow when small particles, droplets, or micelles are suspended in the solvent. This is the conception of Einstein as applied impartially by him to suspensions and true solutions of large molecules such as sucrose.

b) The increased shear imposed upon the solvent, (or rather, solution) for a given amount of flow by droplets of an emulsified liquid that contains a relatively smaller proportion of solvent. This is the usual emulsoid conception, associated with the teaching of Wo. Ostwald, which assumes partial miscibility of the two liquids.

c) The increased shear imposed upon the solvent for a given amount of flow when small rigid colloidal particles or micelles cohere to form loose or open aggregates suspended in the solvent. These larger structures practically immobilise the solvent which they embrace. This is the view held by the writer and by Loeb.

d) An additional effect, only occurring in concentrated suspensions or emulsions, or where the aggregates ramify throughout a large part of the solution, is the deformation of the droplets or aggregates caused by the mutual interference of the particles which are necessarily brought into contact during shear. Much of the work of E. C. Bingham on viscosity and plasticity has lain in this field. Hatschek has developed an elegant treatment of the case of the deformation of liquid droplets in concentrated emulsions during shear.

He deduced the formula $\frac{\eta}{\eta_0} = \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1}$, where A is the ratio between the total volume of the emulsion and the volume of the dispersed droplets, the formula being applicable to cases where A is less than 2. Incidentally he showed that the formation and behaviour of an elastic solid such as a jelly cannot be explained on the basis of a liquid-liquid model. There appears to

---

*Compare preliminary notice in Trans. Faraday Soc., **20**, 22-24 (1924).

be no evidence for regarding the particles of nitro cotton as being liquid either in sol, jelly or gel; they may rather be considered as composed of non-deformable micelles which form aggregates, change in whose structure or orientation will require work to be done.

In the case of a dilute suspension (see explanation (a) above), Einstein[1] and Hatschek[2] have independently deduced formulae which ascribe the enhanced viscosity entirely to the extra movement required of the solvent. Their formulae are $\eta = \eta_0(1+kv)$ where v is the fraction of solid present by volume and k is a constant which Hatschek thought would be 4.5; Einstein found it as 1 and afterwards altered it to 2.5. The formulae agree in relating the enhanced viscosity to the total bulk of the particles independent of their degree of subdivision. This formula holds to a certain extent, but it is usually necessary to postulate a larger bulk of particles than that which corresponds to their pure dry condition. This is ascribed to solvation of the particles and the conception of solvation and enhanced viscosity arising therefrom has taken a firm hold on present-day chemists.

Hatschek's interpretation of viscosity has not in practice discriminated[3] between (a), (b) and (c). In discussing the high viscosity of very dilute solutions of reversible colloids such as proteins and nitro cotton, where according to his formula the viscosity far exceeds that ascribable to the volume of the dry colloid, this is ascribed to "solvation" although it would involve the greater part of the liquid present. This is however not true solvation.

It does not appear to the writer to be legitimate to treat as solvation solvent that is included in liquid droplets of an emulsion, as in (b), or merely entangled in a ramifying aggregate, as in (c). The effects observed under (a) and (c) are of different orders of magnitude. In the present case we know for example, from our experiments on sorption, that the true solvation of nitro cotton does not exceed an amount of solvent equal to the weight of nitro cotton itself, and the excess viscosity due to the increase in volume of the nitro cotton caused by this true solvation is negligible in comparison with the actual viscosities observed. For example, if the nitro cotton in 1% solution in any solvent of approximately unit density is anhydrous and is of density[4] 1.67 the viscosity slope would be 0.012; if hydrated to unit density it would still be only 0.02.

In place of such low viscosity slopes as 0.01 or 0.02 we get values up to several hundred fold greater. In other words, the apparent viscosity of such solutions as nitro cotton is of a different order of magnitude from that ascribable to simple massive particles according to the principles developed by Einstein and Hatschek; even solvation or the assumption of a film of solvent enveloping and clinging to each particle is wholly inadequate as an explanation.

If Einstein's and Hatschek's formulae are strained beyond the limits in order to explain the high apparent viscosity of these dilute solutions, it is impossible to go further than to assume that the fractional volume v is equal to unity; that is, that the whole volume of the solution is ascribed to the particles themselves: and yet this impossible extreme does not suffice. The formulae thus give at the utmost a viscosity slope of 0.54 (Einstein) or 0.74 (Hatschek), whereas the observed slopes are often very many times greater.

---

[1] Ann. Physik, (4) **19**, 289 (1906).

[2] Kolloid-Z., **7**, 301 (1910); **8**, 34 (1911); Trans Faraday Soc., **9**, 80 (1913).

[3] See for example Biochem. J., **10**, 330 (1916).

[4] J. Soc. Chem. Ind., **26**, 449 (1907).

Of course Hatschek would at once apply his cube root formula if the disperse phase were assumed to occupy over 50% of the total space and this would account under such conditions, for any required viscosity slope up to infinity. However, we have the experimental fact that these enormous viscosity slopes are observed in very dilute solution and that they are, if anything, still higher in extreme dilution; so that, if this way out were to be accepted it would be necessary to assume that in each of these successive low dilutions the greater part of the solvent must be dissolved in the disperse phase. In other words, it would be necessary to assume that in extreme dilution the composition of the two phases was almost indistinguishable and yet that they did not mix but formed a concentrated emulsion.

Hence, we can with confidence conclude that the structure of these dilute emulsoid sols is not at all that contemplated in the deduction of the Einstein and Hatschek formulae. The argument here developed appears to involve further conclusion that viscous sols such as nitro cotton do not exhibit true viscous flow.

Hatschek's formula is however beautifully confirmed for the case of true emulsions. A striking illustration of this is the viscosity exhibited by suspensions of blood corpuscles in which each corpuscle is separate although in the most concentrated suspension the corpuscles occupy 90% of the total volume of the system[1]. The relative viscosity observed 30.5 is precisely that predicted by the Hatschek cube root formula. Although this relative viscosity appears high, it is incomparably lower than that which would be exhibited in any corresponding solution of nitro cotton where we believe that the colloidal particles are not separate but are linked together to form ramifying aggregates, which produce an apparent viscosity far greater than that accounted for by their real volume. If the relative viscosity of a dilute solution (say 3%) of nitro cotton, is 1000 and the attempt were made to interpret this as an emulsion according to the Hatschek formula it would have to be assumed that the nitro cotton occupied 99.8% of the total volume leaving only 0.2% for the solvent as continuous medium. For a solution of nitro cotton only a little more concentrated the total volume of the "continuous medium" becomes infinitesimal. However, we know from direct sorption experiments that nitro cotton does not take up more than its own weight of solvent and that therefore this extraordinary emulsoid explanation is inadmissible.

Hypothesis (c) is advocated by the writer to explain these enormous viscosities which are evidently so far beyond the effects of solvation or immobilised solvent films; (although both probably occur, they are of minor importance). The explanation is that given in paragraph (c) and (d) at the beginning of this section; that is, that ramifying colloidal aggregates embrace and practically immobilise large portions of the solution. This necessarily involves interference between these particles and deformation of these structures when the solution is made to flow. It is equally evident that if each of the regions of the solvent which is immobilised by the presence in it of one or more ramifying aggregates behaves, to a certain extent, as an entity, that the apparent viscosity of the whole system must have some such form as that provided in the empirical Arrhenius formula and explained on mechanical and geometrical grounds in the Hatschek cube root formula.

---

[1] Kolloid-Z., **27**, 164 (1920).

It is clear therefore that the chief source of viscosity is ascribable to the formation of ramifying aggregates, and that the best solvent is that which most efficiently dismembers them. The highest viscosity slopes do not reflect high solvation, but probably the contrary; that is, insufficient solvation to disintegrate the particles.

Before proceeding to discuss the hypothesis of neutral colloids it should be pointed out that the preceding discussion has largely justified the use of relative viscosity (η/η_0) compared with that of the solvent as a correct formulation of results of viscosity measurements in various solvents since in all cases enhanced flow is required of the solvent itself.

We have studied the viscosity of nitro cotton only in diluted solution and at temperatures usually above gelatinising temperature. Nevertheless, we are justified, if our conception of viscosity as due to ramifying aggregates is correct, in deducing therefrom the behaviour of nitro cotton at concentrations and temperatures where it does form hard gels.

Further corroborative evidence is to be found in the parallelism between the mechanical strength of cotton hairs on the one hand and the viscosities of solutions of the same cotton in cuprammonium[1]. This parallelism is well known to apply extensively between various solutions derived from different samples of cellulose when compared in a series of different solvents, even after the samples of cellulose have been submitted to drastic treatment and esterified.

B. *Further evidence that the apparent viscosity is not the true viscosity even when fully reproducible.*

Different specimens of nitro cotton of similar composition give different viscosities and the temperature coefficient of viscosity is extremely large. We have to enquire whether the viscosity we have measured at 55° is a true viscosity independent of the rate of shear and method of measurement. We know of no single solution of any cellulose ester for which it has been actually demonstrated by experiment that true viscosity exists. Wherever in our own work or in the recorded literature (as far as we know) any direct test has been applied, the flow was found to be dependent on the type of viscometer and the apparent viscosity was not a constant independent of the rate of shear. In Mardles' work on cellulose acetate the Poiseuille tube, the falling ball, and the Störmer rotating cylinder not only gave different numerical values, but the viscosity-concentration curves differed even in form.

---

[1] Farrow and Neale: Shirley Inst. Mem. **3**, 67 (1924); J. Text. Inst. **15**, 157 (1924).

Bingham and Hyden[1] studied nitro cotton (12.1% nitrogen) in acetone and by extrapolation of results with 7.708% solution in acetone at only 5°, 20° and 35° concluded that the deviation from proportionality between actual flow and shearing stress would probably disappear at 43° and he states that there is nothing in his experiments "inconsistent with the view that this 'transition point' is independent of the concentration." His actual data however for 4.966% at 20° and 35° similarly extrapolated point to 60°. His data for 3.98% at 10°, 20°, 30° and 40° point to 70°. In other words all actual measurements gave a distinct deviation from Poiseuille's law and thus do not show a true viscosity as defined by all physicists since 1860. Bingham and Hyden found it possible within their experimental error to obtain a proportionality between flow and shearing stress if for each concentration at each temperature a small arbitrary amount (different for each series) was subtracted from the actual shearing stresses. These corrections he called friction or yield value and it is to be noted that their evaluation involved fairly big extrapolations. The significance ascribed to the yield values was to the effect that at lower shearing stresses no flow at all would occur. However, it must be remembered that no such phenomenon has ever been observed with sols of cellulose ester and there seems to be no cogent theoretical necessity for the existence of such yield values. Bingham[2], in a later paper now finds that even the apparent yield values for a given solution as obtained by extrapolation vary widely with the dimensions of the viscometer.

Hatschek[3] reiterates the result of his work with Miss Humphrey[4] in which they used a suspension of granules of starch in a mixture of toluene and carbon tetrachloride. Here there is no question of gelatinising particles but the viscosity as measured diminishes with increasing rate of shear and the highest concentrations show this most clearly. Hatschek regards the behaviour of his suspensions as a part of the typical behaviour of all sols including the so-called emulsoid sols such as for example our solutions of nitro cotton. He does not ascribe it like Bingham to plasticity nor to elasticity but considers that each particle is covered with a thin layer of clinging liquid which is diminished in thickness as the shear increases. He is inclined to extend this explanation of variable viscosity to all colloidal systems; but compare the preceding discussion.

L. E. Smith has carried out the following experiments (Table I) to investigate the relation between rate of flow in the viscometer and the head of pressure employed. It is seen that in every case there is a lack of strict proportionality between efflux and shearing stress, and that the apparent viscosity is not a true viscosity.

---

[1] Franklin Inst. **194**, 731 (1922).

[2] "Colloid Symposium Monograph," **2**, 210 (1925).

[3] Kolloid-Z., **37**, 25 (1925).

[4] Proc. Phys. Soc. London, **28**, 274 (1916).

TABLE I

Relation between head of pressure and rate of flow in the viscometer for solutions of nitro cotton. L. E. Smith.

Time (secs)	Pressure cms Hg	$\frac{p.t}{1000}$	$\frac{1}{10,000t}$
Benzyl formanilide at 25.0°C			
897	79.4	71.2	11.15
1425	52.0	74.1	7.02
Therefore friction = 5×10^8 cms. Hg			
Ethyl formanilide at 55.0°C			
326.4	84.7	27.65	30.65
381.2	72.6	27.67	26.24
496.4	56.45	28.03	20.14
648.4	43.6	28.28	15.41
1008.0	28.65	28.87	9.93
2357.0	12.2	28.77	4.24
Therefore friction or yield value = 2.5×10^8 cm. Hg.			
Benzyl phenyl urethane and phenyl urethane mixture at 55.0°			
33.2	78.3	2.60	3.00
36.8	72.75	2.68	2.72
38	69.2	2.63	2.63
43.8	61.75	2.71	2.28
50.4	58.05	2.77	1.98
54.0	51.6	2.78	1.85
63.4	44.6	2.83	1.54
65.0	43.7	2.84	1.54
68.8	40.85	2.81	1.45
81.6	35.75	2.92	1.23
Therefore friction or yield value = 5×10^8 cms. Hg.			

Even if the yield value were found to be negligibly small or within the limits of experimental error, this would not invalidate the suggestion here advanced that the chief source of viscosity is the mutual interference of the loose aggregates of the primary micelles; it would merely show that they were readily deformed and could slip past each other easily.

C. Theory of neutral colloids or solvated micelles capable of aggregation.

The study of soap solutions in this laboratory has established the fact of aggregation of molecules to form a colloidal unit or micelle. These micelles may be of various kinds. In the past great attention has been given to the role that electrical charges play in the stabilistaion of such particles and this is the usual standpoint from which the so-called suspensoid colloids are discussed. The extreme and most interesting case is the ionic micelle which is essentially an aggregation of fully charged ions. The writer is however convinced that the most important micelles are those in which electrical charge plays but an insignificant role. These are the neutral micelles or neutral colloids exemplified by undissociated soap and sols of nitro cellulose, and which according to Laing and McBain[1] are the particles from which the gel structure of soap solutions are made up.

The stabilising agent in neutral micelles is solvation which gives the surface of each micelle sufficient degree of similarity to the solvent medium. It is common knowledge that compounds of similar character such as hydrocarbons are mutually soluble. Giles and Salmon[2] in a significant study of sols of silver in stearic acid have shown that stabilisation in this non-ionising solvent is due to a coating of each silver particle with silver stearate, the stearate end of each molecule being directed outwards.

A nearly perfect solvent would be one in which the complicated structure of fibres of nitro cotton would be completely reduced to its constituent units; that is, into separate solvated colloidal particles or neutral micelles all existing independently of each other and for such a solvent the viscosity slope would be between 0.01 and 0.02 (of course a still more perfect solvent might be found in which the nitro cotton dissolved as separate molecules, i.e., a crystalloid but no such solvent is known).

The conception here put forward is that the nitro cotton fibres are made up of micelles which are linked together at various points by bonds of residual affinity or chemical valency, these bonds vary greatly in nature and strength. Disjunction of these bonds is brought about by combination with solvent molecules which by adding on satisfy the residual affinities. The action is the same as the loosening of a glass stopper by the penetration of a film of oil which separates the two glass surfaces by uniting with each of them. An exact parallel is also found in the action of a soap solution in separating dirt from a fabric through the soap combining with the fabric and with the dirt according to the equation suggested by the writer in 1920:[3]

$$\text{Fabric}:\text{dirt}+\text{soap}=\text{fabric}:\text{soap}+\text{dirt}:\text{soap}$$

Definite chemical groups are required for combination with definite portions of the molecules on the exposed surfaces of the micelles. The best practical solvents are those which are most effective in disuniting the bonds between the micelles. The disjunction fails in the case of non-solvents although they may combine to a certain extent and disunite a few bonds without releasing the whole aggregation. Poor solvents effect it slowly and not to so great an extent as good solvents. The so-called degradation or ageing of nitro cotton discussed in the previous paper must be largely progressive dismemberment.

This conception shows clearly how apparent viscosity of various solutions of nitro cotton is to be explained. It is due to the presence of loose ramifying aggregates of micelles. The best solvents are those in which dismemberment proceeds furthest through solvation of the various points of affinity.

---

[1] J. Chem. Soc., **117**, 1507 (1920).

[2] J. Chem. Soc., **123**, 1597 (1923).

[3] "Third Colloid Report of the British Association," 26 (1920).

Poorer solvents are those in which dismemberment is less complete and the apparent viscosity therefore much higher. Similarly there is a complete series of gradations among non-solvents from substances which are completely indifferent to nitro cotton, if any such exist, through those which combine more up to those where just sufficient bonds are loosed to form colloidal sol, and the non-solvent just becomes a solvent.

It is also clear why mixtures are so very frequently much better solvents than pure substances, because a variety of chemical groupings is offered for union with the corresponding bonds.

There is not the least uncertainty about the existence of combination between nitro cotton and various substances, more especially the good solvents. Reid in an unpublished ebullioscopic study has proven the fact of combination and all our evidence from the sorption of vapours of solvents and non-solvents by nitro cotton and from sorption by nitro cotton of solvents from solution in diluents shows a graduation in the strength of the various bonds. The affinities are very different, some strong, others remarkably weak. Hence, anything which lowers the availability of the solvent markedly decreases the combination. Very slight alternations are necessary to effect important changes. Thus a small amount of diluent would remove the solvent from the localities of weakest affinity, owing to the slight lowering of the chemical potential of the solvent.

The bonds between the particles are restored if the suitable localities of those particles are deprived of their chemical complements (not necessarily molecules of the solvent) whether by change of temperature addition of diluents, lowering of vapour pressure, change of concentration or direct chemical action.

The formation of a jelly from a sol need not involve any extensive alteration in the micelles existing in the sol, even if in the sol they exist quite independently of each other. Only a few points have to be deprived of their chemical complement for a loose union between adjacent micelles to occur and a jelly structure to result. In the case of soap it has been shown that the micelles in sol and jelly are practically identical and the conductivity of sols of gelatine containing salt or of agar containing salt has been shown by Arrhenius and Hatschek respectively to be practically unchanged on formation of a jelly. In a definite sense the degree of dispersion may be equally great in a sol and in a jelly. Unpublished work by Salmon and Manning explains the action of urea in depriving gelatin of its power to set to a jelly, combination of the urea with the gelatin replacing the usual linking up of the terminal amino and carboxyl groups. I venture to suggest that the presence of elasticity in a colloidal solution is a specific positive test for the presence of ramifying aggregates.

The standpoint here advocated lends a fuller significance to lyophile and lyophobe colloids respectively; namely, those in which the disperse phase has such an affinity for solvent that sols can and cannot be formed spontaneously.

To sum up, the linking together of colloidal particles or micelles to form larger structures is caused by bonds of union which are at least as local and specific as the processes operative in adsorption or residual affinity. These bonds are loosed by the substitution in them of various chemicals. This generalised form of solvation is the essential factor in gelatinising and dissolving nitro cotton and in explaining the apparent viscosity of the resulting systems. Only when aggregation is on an excessively coarse scale can mechanical means be effectually employed towards breaking it up. Otherwise, the one great operative force to be taken into account is the solvation, physical or chemical or both, of the molecules in the colloidal micelle.

Department of Physical Chemistry,
The University,
Bristol, England.
September, 1925.

EQUILIBRIUM IN THE SYSTEM ARSENIC PENTOXIDE, BARIUM OXIDE, WATER. (ACID SECTION)*

BY STERLING B. HENDRICKS

The increasing use of alkaline arsenates as insecticides necessitates a more complete knowledge of the chemical properties of these substances. The following research describes the results obtained from a study of the acid section of the system BaO, As_2O_5, H_2O. Since equilibrium conditions are not rapidly established in basic solutions the basic section of this system will be reported later.

Preparation of Materials.—$Ba(OH)_2 . 8H_2O$ was prepared by recrystallizing "C.P." reagent from CO_2—free distilled water. It gave a negative test for Cl^-, CO_3^{--}, and NO_3^-. $As_2O_5 . 4H_2O$ was prepared by the method previously described by C. M. Smith[1].

Experimental Procedure.—100 cc. paraffined cork stoppered oil sample bottles were used for experimental vessels. Solutions of known concentration, containing some of the solid phase, were placed in these and were then immersed in a thermostat regulated at 30° ± .1°. Equilibrium conditions were determined by analysis of the solutions at intervals of one week. Analyses were made in the manner given below.

Analysis.—The densities of the solution were determined by means of a pycnometer, the temperature being 20°. The barium was determined by the sulfate method, the ignited $BaSO_4$ being moistened with conc. H_2SO_4 and reignited in order to remove chloride impurities. The arsenic was determined by titrating the I_2 liberated from an iodide in conc. HCl solution, accurately standardized $Na_2S_2O_3$ solution being used.

Since any attempt to dry or wash the solid phase would probably have resulted in hydrolysis or dehydration, it was necessary to use the method of analysis of wet precipitates[2] in order to determine the compositions of the solid phases. Since there were slight experimental errors involved in the analysis, the exact point of intersection of several lines determining the composition of a solid phase could not be determined by graphical means. The most probable point of intersection of several lines was assumed to be that point at which the sum of the squares of the perpendicular distances to the lines was a minimum. Since the two points determining a line were very close together in the case of the more acid solutions, it was necessary to identify the solid phases present by microscopic means. The results of the analyses are given on pages 250-251.

The stable phases and the solutions in equilibrium with two of them are: $BaHAsO_4 . H_2O$ and $BaH_4(AsO_4)_2 . 2H_2O$, solution, 16.65% BaO and 28.01% As_2O_5; $BaH_4(AsO_4)_2 . 2H_2O$ and $3As_2O_5 . 5H_2O$, solution 72.04% As_2O_5 and a trace of BaO; $BaHAsO_4 . H_2O$ and some more basic arsenate, probably $Ba_3(AsO_4)_2 . x H_2O$, solution, .025% BaO and .03% As_2O_5. $3As_2O_5 . 5H_2O$ was assumed to be the solid phase present in the most acid solution, since the analysis of the wet solid gave proof that $As_2O_5 . 4H_2O$ was not present. Menzies and Potter[1] reported these oxides, $3As_2O_5 . 5H_2O$ being stable above 29°, thus explaining the conversion in this experiment. The constant solution containing .025% BaO and .03% As_2O_5 with $BaHAsO_4 . H_2O$ and $Ba_3(AsO_4)_2 . x H_2O$ as a solid phase gave no evidence of existing in equilibrium with $Ba_5H_2(AsO_4)_4 . x H_2O$, the analogous calcium compound has been recently prepared. These compounds with the exception of the latter have been previously described[2].

---

*Contribution from the Kansas State Agricultural College.

[1] J. Am. Chem. Soc., **42**, 259 (1920).

[2] Bancroft: J. Phys. Chem., **6**, 178; Browne: 287 (1902).

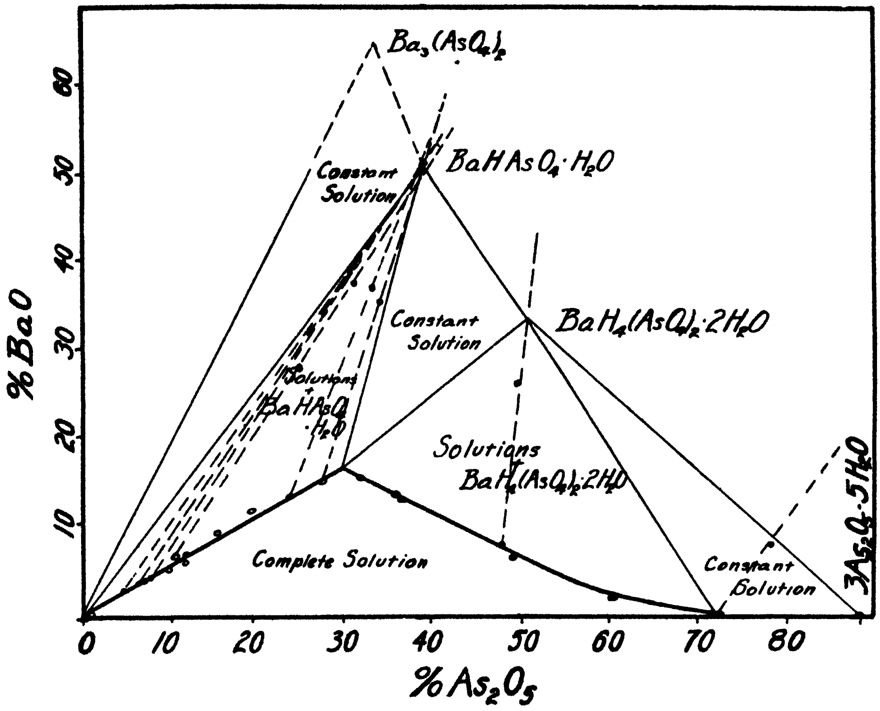


FIG. 1

Preparation of Barium Arsenates.—Since most of the methods of preparation of barium arsenates previously described were found to be unsatisfactory, the older methods have been tested and new methods devised. Mono barium arsenate has previously been described by Mitscherlich[3] by adding $Ba(OH)_2$ to conc. H_3AsO_4, which is essentially precipitation beyond the invariant point in the previous diagram, Fig. 1. The following method gave satisfactory

---

[1] J. Am. Chem. Soc., **34**, 1469 (1912).

[2] Gmelin Kraut: "Handbuch anorg. Chem.", 3 II, 584.

[3] Gmelin Kraut: loc. cit.

TABLE I

Analysis of equilibrium experiments in the system BaO, As_2O_5, and H_2O

	Solutions.						Solids			
Exp. No.	Density	%BaO	%As_2O_5	Mol ratio	Grs. BaO per L.	Grs. As_2O_5 per L.	%BaO	%As_2O_5	Mol ratio	Comments
1	1.003	.22	.002	136.8	2.22	.03	51.64	23.10	3.55	"Solid solution" probably.
2	1.002	.11	.003	57.3	1.07	.03	44.45	21.75	3.07	
3	1.001	.03	.034	1.02	.23	.34	45.89	22.73	3.01	Solid phases $BaHAsO_4.H_2O$ and $Ba_3(AsO_4)_2$. Two months required to establish equilibrium.
4	1.001	.03	.034	1.20	.27	.34	45.24	23.77	2.86	
5	1.001	.03	.031	1.20	.25	.31	46.41	25.62	2.73	
6	1.001	.03	.032	1.16	.25	.32	35.34	20.27	2.61	
7	1.002	.02	.032	1.37	.20	.32	42.11	26.02	2.43	
8	1.002	.03	.029	.93	.27	.29	42.13	28.77	2.21	
9	1.067	2.63	3.98	.99	28.06	42.46	38.34	29.60		Solid phase—$BaHAsO_4.H_2O$
10	1.094	3.60	5.86	.92	39.38	64.10	34.10	27.24		
11	1.105	4.44	7.19	.92	49.01	79.50	37.31	29.48		
12	1.108	4.04	6.72	.90	44.76	74.45	31.94	25.50		
13	1.117	4.36	7.26	.90	48.59	81.09	38.01	30.22		
14	1.151	5.49	9.28	.89	63.15	106.71				
15	1.176	6.25	10.56	.89	73.49	124.2	27.83	24.13		
16	1.188	6.62	11.27	.88	78.64	133.9				

TABLE I (continued)

Analysis of equilibrium experiments in the system BaO, As_2O_5, and H_2O

		Solutions					Solids			
Exp. No.	Density	%BaO	%As_2O_5	Mol ratio	Grs. BaO per L.	Grs. As_2O_5 per L.	%BaO	%As_2O_5	Mal ratio	Comments
17	1.281	6.98	11.12	.94	82.50	131.5	Three weeks required to produce equilibrium. Solid phases examined microscopically, proved to be $BaHAsO_4 . H_2O$.			
18	1.271	9.46	14.92	.95	120.2	189.8				
19	1.357	11.67	18.52	.94	158.1	251.4				
20	1.474	13.59	22.95	.90	200.1	338.0	36.95	32.52		
21	1.592	15.37	27.26	.85	244.8	434.5	35.01	33.62		
22	1.694	15.65	31.17	.75	265.2	528.0	Two weeks required to establish equilibrium. Solid phases $BaH_4(AsO_4)_2 . 2H_2O$.			
23	1.704	13.70	35.10	.58	233.7	597.8				
24	1.719	13.35	35.87	.56	229.3	616.2				
25	1.809	7.53	47.27	.24	136.2	855.1	26.83	40.25		
26	1.817	6.56	48.48	.20	119.1	880.0				
27	2.150	trace	68.40	—	trace	1471.0				
28	2.280	trace	72.04	—	trace	1644.0	8.91	77.60		$3As_2O_5 . 5H_2O$ and $BaH_4(AsO_4)_2 . H_2O$ are the solid phases. Solid phase is $BaH_4(AsO_4)_2 . 2H_2O$.
29	1.869	trace	59 44	—	trace	1110.0				

results; melted $Ba(OH)_2 . 8H_2O$ was poured into an excess of 45% H_3AsO_4, the hard, well-crystallized solid, was removed, dired at 130°, and analysed. The analysis gave 36.30% BaO, 55.45% As_2O_5, 8.25% H_2O; calculated for $BaH_4(AsO_4)_2$ 36.58% BaO, 54.83% As_2O_5, 8.57% H_2O.

The following table summarizes the results obtained in the investigation of $BaHAsO_4 . H_2O$.

TABLE II

Method used	%BaO	%As_2O_5	Ratio BaO/As_2O_5.
Excess $H_3AsO_4.Ba(OH)_2$ added drop by drop.	41.73	32.89	1.90
Excess $Ba(OH)_2 . H_3AsO_4$ solution added drop by drop.	51.09	37.56	2.03
$H_3AsO_4 . Ba(OH)_2$ solution added drop by drop until the solution was neutral to phenolphthalein. Refluxed for four hours.	51.43	37.71	2.04
Excess $BaCl_2$ disodium arsenate solution added to boiling solution.	51.82	36.68	2.12
Impure dibarium arsenate dissolved in dilute HCl and reprecipitated by the slow addition of dilute ammonium hydroxide.	51.32	38.20	2.01
Disodium arsenate, dilute solution, saturated with dibarium arsenate in the cold, heated to boiling and filtered.	51.71	38.68	2.00
Calc. for $BaHAsO_4 . H_2O$.	51.93	38.93	2.00

The last method was devised on the basis of the decrease in the solubility of $BaHAsO_4 . H_2O$ with an increase in temperature. The filtrate from the first solution deposited large crystals, .5 cm. long, having a common index of refraction = 1.635. This table illustrates the necessity of preventing the more basic compounds from precipitating from the solutions.

The methods previously described for the preparation of $Ba_3(AsO_4)_2$ proved to be unsatisfactory. Alkaline hydrolysis of $BaHAsO_4 . H_2O$, with NH_4OH, gave $BaNH_4AsO_4$ in some cases and but rarely gave $Ba_3(AsO_4)_2$[1]. It was hoped that this system would prove to be similar to a similar system of lead[2], but it proved to be quite different.

Dibarium arsenate, prepared by the sixth method given in Table II and containing 38.04% As_2O_3 and 51.60% BaO, was subjected to hydrolysis by NH_4OH solutions. In order to determine whether ammonia entered the solid phases or not, preliminary hydrolytic experiments were made with solutions varying from 1 to .01 M. Examination of the solid phases, after careful washing with acetone, showed the absence of ammonia, the Nessler test was used. In the experiment as summarized in Table III one gram samples of the dibarium arsenate were treated with CO_2-free NH_4OH (prepared by distillation in the presence of $Ba(OH)_2$), the arbitrary dilution being .0383 N.

---

[1] Salkowski: J. prakt. Chem., **104**, 143 (1868); Lefevre: Ann. Chim. Phys., **27**, 13 (1892).

[2] Smith and McDonnell: J. Am. Chem. Soc., **38**, 2366 (1916).

Referring to Table II one can see that the first additions of NH_4OH resulted in a constant solution in equilibrium with $BaHAsO_4 . H_2O$ and $Ba_3(AsO_4)_2 . x H_2O$. The disappearance of the dibarium arsenate is shown by the breaks in curves; the lower curve is a rectangular hyperbola showing that hydrolysis of $Ba_3(AsO_4)_2$ does not take place. Analysis of the dried solid phases from several experiments supposed to contain the tribarium arsenate gave the following results: BaO, 66.60%; As_2O_5, 33,11%; calculated for $Ba_3(AsO_4)_2$; BaO, 66.67%; As_2O_5, 33.33%.

TABLE III

Exp. no.	Cc. NH_4OH used.	Grs. As_2O_5 removed.	Grs. As_2O_5 removed per liter.	Mol ratio in solid phase BaO/As_2O_5.
1	40	.0425	1.0613	2.25
2	50	.0504	1.0084	2.30
3	60	.0596	0.9936	2.37
4	80	.0830	1.0369	2.55
5	90	.0881	0.9788	2.59
6	100	.1005	1.0050	2.71
7	120	.1165	0.9713	2.86
8	130	.1264	0.9722	2.98
9	140	.1291	0.9225	3.01
10	150	.1285	0.8569	3.00
11	170	.1294	0.7612	3.01
12	200	.1331	0.6657	3.04
13	210	.1275	0.6075	3.00
14	300	.1308	0.4360	3.02
15	400	.1340	0.3350	3.03
16	440	.1305	0.2966	3.00
17	infinite	trace	trace	3.00

Control field tests using commercial barium arsenate as a dust are now being carried on by the Southern Field Crops Investigation Laboratory of the Bureau of Entomology, the boll weevil (Anthonomus grandis Boh) being used as the experimental insect. Preliminary results show that its toxicity is as great as that obtained from commercial calcium arsenate, the poison used at the present time.

I wish to thank Dr. H. H. King of the college and Mr. C. M. Smith of the Bureau of Chemistry, Washington, D. C. for assistance given to me during the course of this research.

Summary

The stable compounds in the acid division of the system BaO, As_2O_5, H_2O at 30° are $BaH(AsO_4) . H_2O$, $BaH_4(AsO_4)_2 . 2H_2O$, and $3As_2O_5 . 5H_2O$.

Alkaline hydrolysis of $BaHAsO_4 . H_2O$ gave $Ba_3(AsO_4)_2 . x H_2O$. Methods for the preparation of other arsenates are described.

Pasadena, California.

ANOMALOUS FLOCCULATION IN COLLOIDAL CLAYS AND SOILS

BY F. HARDY

Introductory

Anomalous flocculation is the term applied by Comber[1] to denote the particular behavior of aqueous suspensions of colloidal clay towards lime. According to the isoelectric point theory, aqueous disperse systems of electronegative colloids should be stabilized, not flocculated, by small additions of alkali. Clay suspensions, however, are rapidly flocculated by calcium hydroxide, though markedly stabilized by hydroxides of alkali metals and ammonium. By a series of critical experiments with soils, Comber was able to demonstrate that fine silt belongs to the suspensoid class of colloids, whilst clay, though not necessarily composed entirely of emulsoid matter, consists of particles so heavily protected by emulsoid matter, that it behaves as an emulsoid colloid[2].

In order to explain anomalous flocculation, Comber has suggested that a chemical interaction takes place between the emulsoid material and its flocculant[3]. The fact that silicic acid in aqueous dispersion reacts with calcium hydroxide, or with neutral calcium salt in the presence of soluble alkali hydroxide, to form a flocculant precipitate of calcium silicate, is adduced as evidence that a similar reaction may account for the anomalous flocculation of siliceous clay by lime. Hydroxyl-ion peptizes the emulsoid protection of the clay particles; calcium-ion unites with, or is "adsorbed" by the highly dispersed silica; the emulsoid loses its intimate relationship with the dispersion medium, and the particles settle, entrained in the voluminous coagulum.

Anomalous flocculation by lime is apparently not confined to emulsoid clay suspensions. Comber's further investigations[4] have shown that aqueous suspensions of aluminium phosphate, ferric phosphate, basic slag, rock phosphate and powdered bones display similar anomality, provided they are initially free from uncombined lime. In certain instances, ignition does not impair the reactivity of the substance sufficiently to prevent its exhibiting anomalous behaviour in flocculation experiments. It therefore appears that emulsoid soil clay possesses some constitutional feature in common with many phosphatic materials.

Recently the writer has extended the scope of Comber's suggestive researches by demonstrating that certain tropical lateritic soils, examined by the methods elaborated by Comber, exhibit marked anomalous flocculation by lime. The lateritic soils studied have been fully described elsewhere[5]. They were two in number. The first is an orange-red subsoil occurring in the upland regions of Barbados. It is a residual clay derived from coral limestone containing andesitic volcanic ash. The second is a dark-red subsoil occurring in the rainy mountainous regions of Dominica, where andesite has been intensely weathered. Both soils are acidic (pH 6.7 and pH 5.9 in 1 to 3 aqueous suspension); they contain traces only of organic matter and lime, but are rich in alumina and ferric oxide. They also contain appreciable amounts of silica. Their aqueous suspensions in all concentrations settle rapidly; they are stabilized markedly, however, by the addition of relatively small but different amounts of soluble alkali, such as sodium hydroxide and sodium carbonate. In the field, the soils, in common with lateritic soils in general, occur in a highly aggregated condition, so that water percolates readily through them.

---

[1] J. Agr. Sci. 10, 425 (1920); Trans. Faraday Soc., 17, 349 (1922).

[2] J. Agr. Sci. 10, 426-430 (1920).

[3] J. Agr. Sci. 11, 450 (1921); Trans. Faraday Soc., 17, 349 (1922).

[4] J. Agr. Sci. 12, 372 (1922).

[5] F. Hardy: J. Agr. Sci 13, 243, 340 (1923).

The chemical constitution of the colloidal matter of clays and soils is uncertain. Conventional chemical analysis merely expresses the fact that inorganic soil colloids are mainly composed of varying proportions of water, silica, alumina and ferric oxide. Whether these components are simply mixed, or are combined to form colloidal complexes or true compounds, cannot be decided by precise experimental methods. Nevertheless, there is sufficient evidence to prove that many highly siliceous clays and soils contain free hydrous silica, and that many laterites contain free hydrous alumina and free hydrous ferric oxide. A comparison of the physico-chemical features and constitution of these individual substances may therefore lead to a clearer understanding of the properties and behaviour of clays and soils, and in particular to a more exact elucidation of their flocculation phenomena.

I. Hydrous Alumina

Alumina, in aqueous dispersion, behaves as a weak amphoteric electrolyte. The basic and acidic dissociation equations are usually written thus[1]:— $Al(OH)_3 \longrightarrow AlO_3''' + 3H^{\cdot}$ and $Al(OH)_3 \longrightarrow Al^{\cdot\cdot\cdot} + 3(OH)'$. The iso-electric point of alumina has been determined by von Euler and Nilsson[2], who assign to it the pH value 6.50. This implies that the basic and acidic dissociation constants are numerically equal[3] when the reaction of the aqueous dispersion medium is pH 6.50.

The aluminates are generally regarded as salts of the tribasic acid, H_3AlO_3. Heyrovsky[4] suggests, however, that they are more probably salts of the monobasic acid, $HAl(OH)_4$, or $Al(OH)_3.H_2O$, and that they are really "additive compounds". Sodium aluminate, for example, according to this authority, should be represented by the formula $Al(OH)_3.NaOH$.

The composition and properties of several hydrogels of alumina, prepared under different conditions, have recently been investigated by Willstätter and Kraut[5], who obtained evidence that the different dry hydrogels are true hydrates, containing various molecular proportions of water, and exhibiting diminishing basic and acidic properties with diminishing degree of hydration. Weiser[1] has adduced corroborative evidence of the fact that the reactivity of hydrogels of alumina depends on the degree of hydration, but states that only one true hydrate, namely the trihydrate of alumina, exists. Pascal[2], basing his conclusions on the results of certain magnetometric experiments, maintains that neither the hydrates nor the hydrogels of alumina are to be regarded as aluminium hydroxide, but as various hydrous aluminium oxides, and that, even in solutions of aluminates, aluminium occurs as colloidal oxide. This view is upheld by earlier results obtained by Chatterji and Dhar[3], who found that the electrical conductivity of a solution of sodium hydroxide is not appreciably altered when hydrous alumina is dissolved in it, proving that true chemical combination does not occur, but that the alumina is merely peptized by the alkali. The aluminates thus appear to be adsorption complexes rather than the additive compounds of Heyrovsky.

---

[1] Lewis: "A System of Physical Chemistry", 1, 26 (1921).

[2] Ber. 57, 217; Chem. Abs. 18, 1254 (1924).

[3] Clark: "The Determination of Hydrogen-ions", 25 (1920).

[4] J. Chem. Soc., 117, 1013 (1920).

[5] Ber. 56, 149, 1117 (1923); 57, 58 (1924).

In accordance with these findings, it would perhaps be more exact to express, *in its simplest form*, the dissociation of hydrous alumina thus: $Al_2O_3 . 3H_2O \longrightarrow Al_2O_3 . 3OH' + 3\,H^{\cdot}$, and $Al_2O_3 . 3H_2O \longrightarrow Al_2O_3 . 3H^{\cdot} + 3(OH)' \longrightarrow 2Al^{\cdot\cdot\cdot} + 3(OH)' + 3(OH)'$. Since the chemical activity of hydrous alumina dispersed in water appears to be mainly decided by the degree of colloidal hydration, it follows that the primary cause of reactivity is the ionic dissociation of molecules of water that are held at the surface of the solid phase. The relationship between these bound water molecules and the molecules or atoms comprizing the rest of the colloid is obscure. Evidently few analyses of the structure of hydrous inorganic compounds by X-ray methods have so far been attempted[4]. It appears probable, however, that the elements of water are held by residual valency forces of atoms that form the surface layer of the crystal lattices composing the colloid particles[5]. Irregular orientation of these atoms, resulting from the action of agents of disintegration[6], which produce higher degrees of dispersion at the solid crystal surface, may conceivably increase the hydration capacity, and bring about in the particles of the dispersed phase[7], "a gradual transition from the solid nucleus through stages of gel material to the water". Conversely, alumina hydrogels are known to undergo spontaneous change on standing, becoming gradually crystalline, but not necessarily losing all their water[8]. This process, usually termed "ageing", appears to be mainly a manifestation of atomic rearrangement, whereby the elements of water come to occupy a more stable spacial relationship to the other atoms of the system.

---

[1] J. Phys. Chem. **24**, 505 (1920).

[2] Compt. rend. **178**, 481 (1924).

[3] Discussion Rept. "Physics and Chemistry of Colloids", Dept. Sci. Indus. Res. London, **1921**, 123.

[4] Bragg: "X-rays and Crystal Structure", 303 (1924).

[5] Ruff: Kolloid-Z. **30**, 356 (1922); Mukherjee: Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 103. Bassett: "Fourth Report on Colloid Chemistry", 8 (1922).

[6] Donnan: Presidential Address. Sect. B, British Ass. Adv. Sci., (1923); J. Soc. Chem. Ind. **42**, 900 (1923); Harrison: Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 116.

[7] Comber: J. Agr. Sci. **11**, 450 (1921).

[8] Fricke and Wever: Z. anorg. Chem. **136**, 321 (1924).

We are thus led to regard a particle of hydrous alumina, suspended in an aqueous medium, as a complex colloidal electrolyte, whose reactivity or strength depends on the degree of hydration at the boundary surface. The total area of surface, and consequently the hydration capacity, will depend on the degree of dispersion, or, if we assume that the hydrogel possesses a reticulate structure,[1] on the conformation and porousness of the hydrogel skeleton.

Recent research on emulsoid colloids such as soaps[2], proteins[3], and starches[4], has revealed the existence of complex colloidal ions (the ionic micelles of McBain), which originate through the electrolytic dissociation of neutral colloidal systems dispersed in aqueous media. Such ions, in certain instances, may apparently occur in association with un-ionized colloid. At the isoelectric point, the colloid exists as a non-ionogenic substance. When the hydrogen-ion concentration of the medium is decreased, the colloid behaves as an acid; when increased, it behaves as a base.

In the case of hydrous alumina, whose isoelectric point is pH 6.5, the colloid, when placed in pure neutral water (pH 7.0), should therefore exhibit weak acidic properties, because ionization now tends to proceed in the direction of greater production of hydrogen-ion and complex aluminate-ion. Further increase in hydroxyl-ion concentration, brought about for example, by adding a soluble hydroxide, should enhance this tendency. If the added soluble hydroxide be calcium hydroxide, calcium-ion may simultaneously combine with aluminate-ion to form a calcium-aluminate complex. The electric charges on the colloidal ion will consequently be more or less neutralized[5]; the system will be "weighted"; its stability will be reduced; its relationship to the enveloping liquid will be altered through diminished hydration, and precipitation will tend to occur. By this sequence of events is the term anomalous flocculation defined. Should the added hydroxide be the hydroxide of an alkali metal, accompanied or followed by a neutral calcium salt, calcium-ion may combine in preference to alkali metal ion, because of its lower electroaffinity.[6]

The final result nevertheless, in effect, should be the same. If neutral calcium salt be added before alkali hydroxide, the reaction may be impeded, because the first-formed calcium-aluminate complex may conceivably hinder the further and continued dissociation of the colloidal electrolyte.

---

[1] Wilsdon: Mem. Dept. Agr. India, Agr. Res. Inst. Pusa, Chem. Ser. **6** (1921); F. Hardy: J. Agr. Sci. **13**, 243 (1923).

[2] McBain: J. Am. Chem. Soc., **43**, 426 (1920); "Third Report on Colloid Chemistry", 2 (1920); J. Soc. Chem. Ind. **42**, 615 (1923).

[3] Pauli: "Colloid Chemistry of the Proteins" (1922); Loeb: "Proteins and the Theory of Colloidal Behavior" (1922); Discussion Rept. "Physics and Chemistry of Colloids", 153 (1921).

[4] Samec: ref-Pauli: Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 16.

[5] Donnan has pointed out that coagulation may occur as soon as the potential difference at the interface of a suspended colloid is brought within a certain *critical zone* which may extend considerably on either side of the isoelectric point, (Presidential Address, Sect. B, British Ass. Adv. Sci. (1923); J. Soc. Chem. Ind. **42**, 898 (1923).

[6] Bassett: "Fourth Report on Colloid Chemistry", 9 (1922); Mukherjee: Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 111.

On the acid side of the isoelectric point, complex aluminous cations may combine with acid anions to form salts. According to Pauli[1], a series of oxysalts of aluminium, such as $Al(OH)Cl_2$, $Al(OH)_2Cl$ and $2Al(OH)_3 . Al(OH)_2Cl$, is formed when hydrous alumina is peptized by acids. If the process is further continued, a hydrosol results. Pauli regards this sol as an aqueous suspension of a mixture of oxysalts, ionizing to give a complex cation, together with acid anions, as for example, $3Al(OH)_3 . Al(OH^+)_2/CH_3 . COO^-$, but so far his conclusions have not been experimentally substantiated. In the parallel case of ferric oxide sols, Smith and Giesy[2] have recently shown by the use of the oxygen electrode, that oxysalts have no real existence in such sols.

Most authorities[3] prefer to regard the sols of hydrous metallic oxides as composed of particles of oxide suspended in an aqueous phase, and adsorbing greater or lesser amounts of molecules or ions (water, metallic chloride, hydrogen chloride, hydrogen-ion, chloride-ion), depending on their nature and concentration. This view is based on the widely accepted physical theory of adsorption, which Mukherjee[4], has attempted to place on a fundamental basis by suggesting that adsorption may be an actual attachment of ions to a colloidal surface by chemical forces due to residual valences. Whilst it is highly probable that direct chemical combination often occurs at surfaces, it seems more reasonable to assume in the case of a hydrated colloidal electrolyte such as hydrous alumina, that peptization by acids is the result of the enhancement of its acidic dissociation through the effect of hydrogen-ion, which, when introduced in excess, combines with hydroxyl-ion, produced by the ionizing colloid, to form non-ionizing water molecules. The colloid is thereby removed further from its isoelectric point, the potential difference between its surface and the dispersion medium is increased, and the system becomes increasingly stable. The concurrent effect of the anion of the added acid is probably mainly decided by its specific nature and by its relative electroaffinity. Thus, in particular, if the anion be phosphate-ion, silicate-ion, or aluminosilicate-ion, insoluble complexes may result, and precipitation may occur. Each of these particular cases is entirely analogous to the anomalous flocculation of the negatively-charged colloidal aluminous-ion by calcium-ion, which has already been discussed. If the anion have other identity, its preferential combination and consequent precipitating power, may depend on its relative electroaffinity. Only in dispersions of high acidity may simple aluminium salts, such as the metallic chloride, be produced, giving aluminium-ion. Thus McGeorge[5] was able to demonstrate that free aluminium-ion is present in extracts of acid soils only when the reaction is more acidic than that represented by pH 5.8.

Finally, before the flocculation of *positively* charged ions of alumina, contained in sols or their transition systems, can be effected by the addition of lime, sufficient flocculant must be added, not only to change the reaction of the dispersion medium to the pH value representing the approximate isoelectric point, but also to reverse acidic dissociation into basic dissociation. This necessitates the satisfying of a definite "lime requirement", the magnitude of which will depend mainly on the initial acidity of the system, on the presence of ions already adsorbed, and on the extent of its active surface, that is, on the degree of dispersion and hydration. That such conditions control the successful liming of soils, is well known to soil investigators.

---

[1] Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 14; Adolf and Pauli: Kolloid-Z. **29**, 281 (1921).

[2] J. Am. Pharm. Ass. **12**, 855 (1923).

[3] Bancroft: J. Phys. Chem. **19**, 232 (1915); Browne: J. Am. Chem. Soc., **45**, 297 (1923).

[4] Discussion Rept. "Physics and Chemistry of Colloids", **1921**, 103.

[5] Soil Science, **18**, 1 (1924).

II. Hydrous Ferric Oxide

Like hydrous alumina, hydrous ferric oxide is an amphoteric electrolyte. Whilst its basic properties are prominent, its acidic properties are not so pronounced as those of alumina[1]. The "ferrites" are less easily prepared than their analogues, the "aluminates". As far as the writer is aware, the isoelectric point of hydrous ferric oxide has not yet been determined. The conditions for precipitation of hydrous ferric oxide and of hydrous alumina by alkali, however, are almost identical. Thus, Carr and Brewer[2] found that, in the one case, precipitation commences at pH 5.5 and is complete at pH 8.6, and in the other, at pH 5.5 and pH 7.9. This suggests that the isoelectric points of the two ampholytes are approximately the same.

The state of occurrence of water in hydrous ferric oxide appears to be similar to that in hydrous alumina[3], but only one definite hydrate of ferric oxide has so far been described[4]. This is found in crystalline form as the mineral goethite, $Fe_2O_3 . H_2O$[5], whose amorphous form is limonite[6], and whose anhydrous form is haematite. Other hydrated ferric oxide minerals, according to Weiser, are probably hydrous oxides, containing variable and indefinite amounts of water[7]. Ferric oxide hydrogels possess the characteristic property of instability, being easily dehydrated to the monohydrate, which exhibits no tendency to reabsorb water[8]. This property, which may be termed rapid ageing, finds expression in the well-known method for the quantitative separation of iron from aluminium, in which the hydrogels of the oxides are first precipitated and then boiled with excess of caustic alkali. Alumina hydrogel is thereby peptized, whereas ferric oxide hydrogel is dehydrated and remains in suspension[9].

The yellow, red, and brown colours of hydrous ferric oxide are believed to be due to diminishing degrees of hydration[10]. Weiser[11], however, was able to prepare transition forms of the substance, exhibiting colours ranging from yellow to red, by merely increasing the size of the particles, and Yoe[1] found that red coloured forms could be produced from finely divided yellow particles by agglomeration. There is evidently some close relationship between colour and degree of colloidality in the various types of hydrous ferric oxide, and this should be reflected in the physical and chemical properties of laterites.

---

[1] Caven and Lander: "Systematic Inorganic Chemistry", 316 (1921).

[2] Ind. Eng. Chem. **15**, 634 (1923); Hatfield (**16**, 233 (1924)) gives narrower limits for the stability of the solid phase of hydrous alumina, namely pH 5.7 and pH 7.3.

[3] Weiser: J. Phys. Chem. **24**, 277 (1920).

[4] Posnjak and Merwin: Am. J. Sci. **47**, 311 (1917).

[5] Spencer: Min. Mag. **18**, 339 (1919).

[6] Fischer: abstracted in J. Chem. Soc. **96**, 241 (1909).

[7] J. Phys. Chem. **24**, 277 (1920).

[8] Zsigmondy-Spear: "Chemistry of Colloids", 169 (1917).

[9] Bassett: "Fourth Report on Colloid Chemistry", 18 (1922).

[10] Fischer: loc. cit.

[11] See also Bancroft: "Applied Colloid Chemistry", 205 (1921); Bradfield: J. Am. Chem. Soc., **45**, 965 (1923).

Because of their amphoterism, and the close resemblance between hydrous ferric oxide and hydrous alumina as regards the state of occurrence of water in the hydrogel, the general properties and structure of disperse systems of these emulsoid colloids are markedly similar. Thus, the much-studied ferric oxide sols, in which the dispersed phase is positively charged, conform closely in character to the sols of alumina, and have recently been investigated from similar standpoints[2]. The ampholytic nature of hydrous ferric oxide has been established beyond doubt by the researches of Fischer[3], Powis[4] and Dhar and Sen[5], who have demonstrated that a reversal of sign of charge can be effected in disperse systems of this colloid by simply reversing the reaction of the dispersion medium. It therefore follows that the particular mechanism which has tentatively been propounded to explain anomalous flocculation of hydrous alumina, might equally well apply to the anomalous flocculation of hydrous ferric oxide. In actuality, the process is certainly not so simple as a consideration of the ideal cases suggests, for subsidiary factors, introduced by the presence of extraneous salts and colloidal matter, doubtless modify the sequence of changes that has been described. The precise manner in which such subsidiary factors may affect the flocculation of disperse systems of hydrous ferric oxide, (and of hydrous alumina), has received considerable attention by recent investigators[6]. Although mainly viewed from other aspects, the results obtained are susceptible of explanation in terms of ordinary ionic interaction and mass influence, regard being paid to the relative electroaffinities of the reacting units[7]. In parallel cases, certain irregular results have been shown to be due to an actual entrapping of solutions of unionized electrolytes in the intermicellar spaces of the colloid[8].

III. Hydrous Silica

Hydrous silica differs chemically from hydrous alumina and hydrous ferric oxide in that its acidic properties are much more pronounced than theirs, whilst its basic properties, in most of its reactions, are in entire abeyance.

---

[1] J. Phys. Chem. **25**, 196 (1921).

[2] Malfitano: Z. physik. Chem; **68**, 232 (1909); Neidle: J. Am. Chem. Soc., **39**, 2334 (1917); Pauli and Matula: Kolloid-Z. **21**, 49 (1917); Pauli: **28**, 49 (1921); Weiser: J. Phys. Chem. **24**, 277 (1920); Browne: J. Am. Chem. Soc., **45**, 297 (1923).

[3] Biochem. Z. **27**, 223 (1910).

[4] J. Chem. Soc., **107**, 818 (1915).

[5] J. Phys. Chem. **27**, 376 (1923); Ganguly and Dhar: **28**, 313 (1924).

[6] Neidle, Pauli, Dhar, Browne: loc. cit.; Weiser et al.: J. Phys. Chem. **23**, 205 (1919); **24**, 30, 630 (1920); **25**, 399 (1921); **26**, 665 (1922).

[7] Bassett: "Fourth Report on Colloid Chemistry", 9 (1922).

[8] Wintgen: Z. physik. Chem. **103**, 238 (1922).

Hence hydrous silica is usually not regarded as an amphoteric electrolyte, but as a true acid. Nevertheless, the similarity that exists between compounds of silicon and corresponding compounds of germanium, tin and lead, (especially the halides[1]), suggests that silicon may be considered as a basigenic element of very low electroaffinity. Furthermore, there is some direct evidence in support of the view that hydrous silica is an ampholyte possessing an isoelectric point well on the acid side of neutrality. Thus Lösenbeck[2] has demonstrated by cataphoretic methods that the addition of hydrochloric acid to a silica sol brings about a gradual decrease in the magnitude of the negative charge on the silica particles, and that eventually a stage which appears to be coincident with the isoelectric point of the colloid, is reached. Further additions of hydrochloric acid are stated to cause the particles to assume a positive charge. The pH value of the isoelectric point is apparently not given by Lösenbeck. Schwarz[3] found no evidence, however, of the formation of a definite chemical compound between colloidal silica and hydrochloric acid, but Werner[4] noted that acids exert a powerful peptizing effect on silica hydrogel.

Recently Michaelis[5] has suggested that colloidal electrolytes might be classified into "ampholytoids", "acidoids" and "basoids". He places hydrous alumina and hydrous ferric oxide in the first category, hydrous silica in the second, but can find no examples of the third class If we regard amphoterism as a property possessed in different degree by certain colloidal electrolytes, and manifesting itself in different pH values for their isoelectric points, there would appear to be no particular advantage in this classification, at least insofar as hydrous oxides are concerned.

The state of occurrence of water in hydrous silica, as in the case of the other hydrogels considered, has been the subject of much experimentation and speculation. The characteristic changes in moisture content, vapour pressure, volume and physical properties which silica hydrogel undergoes when dried, are too well known to require repetition[6]. They may perhaps most clearly be explained on the assumption that silica hydrogel possesses a reticulate structure[7], which, when saturated, contains water in two phases, the one adsorbed at the surface of the material comprizing the gel framework; the other filling the intermicellar spaces.

It is generally conceded that no true hydrates of silica exist[8]. Nevertheless, many authorities favour the view that definite silicic acids, such as orthosilicic acid (H_4SiO_4), are present in silica hydrosols and hydrogels[9]. The solubility of silica in water has been measured[1]; the dissociation constants estimated[2]. and the reaction of a silica sol freed from electrolytes has been examined[3], and found to be acidic (pH 6.5).

---

[1] Huddleston and Bassett: J. Chem. Soc., **119**, 403 (1921).

[2] Kolloidchem. Beihefte, **16**, 27 (1922).

[3] Kolloid-Z. **34**, 23 (1924).

[4] J. Am. Pharm. Ass. **17**, 501 (1920).

[5] Kolloid-Z. **31**, 256 (1922).

[6] Zsigmondy-Spear: "Chemistry of Colloids", 137-150 (1917).

[7] Van Bemmelen, Zsigmondy, Bütschli, Bachmann, Anderson and Patrick, Williams: J. Soc. Chem. Ind. **43**, 97 T (1924).

[8] Hutchinson: Ann. Rept. Chem. Soc. London, **9**, 259 (1922); LeChatelier: Compt. rend. **147**, 660 (1908).

[9] Norton and Roth: J. Am. Chem. Soc. **19**, 832 (1897); Schwartz and Sonard: Ber. **53**, 1 (1920).

Other authorities deny the existence of definite chemical compounds of silica and water, and prefer to regard all associations between them as adsorption complexes[4]. The question, however, appears to be mainly one of nomenclature. As in the case of other hydrous oxides, hydrous silica may contain water molecules united with silica in stoichiometric proportions through the agency of "chemical" adsorption forces. These complexes may exhibit acidic properties because of the ability of certain of the combined water molecules to ionize. The splitting off of small units of the adsorption complex (superficial dispersion) may account for the slight solubility of the substance in water.

The reactivity of hydrogels of silica is believed to depend mainly on the degree of hydration. Thus Tschermak, may years ago, demonstrated that the various silicic acids decolourize solutions of methylene blue to an extent varying directly with the number of hydroxyl groups present[5]. Furthermore, it has been proved that the reactivity of quartz is increased by long grinding with water[6]. On the other hand, silica hydrogels rapidly age into hydrophane[7] or into quartz[8].

These many considerations indicate that hydrous silica conforms closely to the type of emulsoid colloid exemplified by hydrous alumina and hydrous ferric oxide. It may therefore also be classified as a colloidal ampholytic hydrous oxide, differing from the others chiefly in that its isoelectric point is of very much lower pH value than theirs.

According to Comber, hydrous silica probably occurs in siliceous soils and clays as a gelatinous matrix binding together discrete mineral grains to form separate compound particles. The grains themselves may exhibit zonal differentiation as regards degree of weathering and hydration; their cores are presumably composed of anhydrous quartz or of siliceous minerals such as felspar. In aqueous suspension, the compound particles may behave as electronegative colloidal ions, because they will assume the properties of the emulsoid material that coats and protects them.

IV. Hydrous Aluminosilicates and Ferrosilicates

During the processes of weathering, the mineral fragments of soils are hydrolysed and hydrated; the soluble bases that are liberated are simultaneously removed by leaching. Hydrous aluminosilicates and hydrous ferrosilicates are frequently present in the residues. A conspicuous end-product of weathering is amorphous kaolinite (clayite, lithomarge, halloysite), which has long been considered by some authorities to be an aluminosilicic acid, forming salts of zeolitic type[1]. The researches of Gedroiz[2] and others suggest, however that zeolites are adsorption compounds, rather than true salts, for they exhibit the phenomena of basic exchange in marked degree. Highly leached clays, such as laterites, contain only traces of alkali and alkaline earth metals, and in extreme cases, appear to consist almost entirely of hydrous alumina and hydrous ferric oxide in a more or less "aged" condition. The majority of lateritic clays also contain silica.

---

[1] Huddleston and Bassett: J. Chem. Soc., **19**, 832 (1897); Joseph and Hancock: **123**, 2022 (1923).

[2] Grünhut: Chem. Abs. **8**, 3829 (1914).

[3] Bradfield: J. Am. Chem. Soc., **44**, 965 (1922).

[4] Lenher: J. Am. Chem. Soc., **43**, 391 (1921); Pascal: Compt. rend. **175**, 814 (1922).

[5] Z. physik. Chem. **53**, 349 (1905).

[6] Bancroft: "Applied Colloid Chemistry", 97, 179 (1921); Lenher: J. Am. Chem. Soc. **43**, 391 (1921).

[7] Bachmann: Chem. Abs. **12**, 1610 (1918); Schwarz and Stöwener: Kolloidchem. Beihefte, **19**, 171 (1924).

[8] Zsigmondy-Spear: "Chemistry of Colloids", 137 (1917).

Certain investigators have recently suggested that aluminosiliceous clays are colloidal ampholytes, and, to support this view, have adduced experimental evidence, based mainly on measurements of hygroscopicity and of settling rates of clay suspensions at different hydrogen-ion concentrations[3]. From their results, values for the isoelectric points as diverse as pH 9.7 (brick clay, Arrhenius) and pH 2.78 (ball clay, Hall), have been derived. Although the validity of conclusions based on such experiments may be questioned, it is now at least generally admitted that hydrous aluminosilicates, (and hydrous ferrosilicates), react as true acids when dispersed in water, and that acidity in mineral soils is mainly due to their presence[4]. If hydrous aluminosilicates be ampholytes, possessing basigenic as well as acidic properties, their aqueous suspensions ought to be increasingly stabilized by strong acids, added in sufficient amount to lower the pH value of the system to the acid side of the isoelectric point or region. Durham's discovery (1874), recorded by Wolkoff[5], is therefore of significance in this connection; he found that "although it requires a very small amount of sulphuric acid to flocculate a suspension of white clay (? kaolin), on further additions of sulphuric acid he reached a point when the suspension did not clarify for a long time". Possibly also, certain results obtained by Bradfield, who examined the relation of hydrogen-ion concentration to the flocculation of a colloidal clay[6], may partly be interpreted in the light of these considerations. The whole question of the possible amphoterism of hydrous aluminosilicates might profitably be re-examined with the aid of physico-chemical instruments of high precision.

Certain aluminosiliceous clays are probably composed mainly of adsorption complexes of hydrous alumina and hydrous silica, rather than true hydrous aluminosilicates in which alumina and silica are present in molecular or atomic combination. It has already been pointed out that hydrous alumina, when dispersed in an aqueous medium of pH value less than that representing the isoelectric point of the colloid, may suffer "anomalous flocculation" by silicate-ion. Mutual precipitation of hydrous alumina and hydrous silica ought therefore, in theory, to occur in an acid medium of pH value lying somewhere between the pH values representing their isoelectric points, and would be complete if the colloids were present in equivalent amount[1]. Under such circumstances, the one colloid occurs as a complex cation, the other, as a complex anion. Similarly, mutual precipitation may occur, under appropriate reaction conditions, in dispersions containing hydrous ferric oxide and hydrous silica, and, indeed, in dispersions containing any assortment of these various hydrous oxides and hydrous aluminosilicates and ferrosilicates, granting that each of these colloidal substances possesses amphoteric properties. The facts that most lateritic clays and soils containing alumina, ferric oxide and silica occur in a highly aggregated condition in the field, and yield aqueous dispersions that rapidly settle, even in the presence of acid in excess, lend support to these conclusions.

---

[1] Mellor and Holdcroft: Trans. Eng. Ceramic Soc. **10**, 10 (1911); Scurti: J. Chem. Soc. **124** 1, 1047 (1923).

[2] See Joffe and McLean: Soil Science, **18**, 1 (1924).

[3] Arrhenius: J. Am. Chem. Soc. **44**, 521 (1922); Hall: J. Am. Ceramic Soc. **6**, 989 (1923).

[4] Crowther: Trans. Faraday Soc., **17**, 317 (1922); Page: Ann. Rept. Chem. Soc. London, **9**, 19 (1922); **10**, 20 (1923); Bradfield: J. Am. Chem. Soc. **45**, 2667 (1923).

[5] Soil Science, **1**, 585 (1916).

[6] J. Am. Chem. Soc. **45**, 1243 (1923).

It ought to be possible to test the various suggestions made in the foregoing discussions by a detailed examination of selected soil and clay samples. In particular, laterites seem to offer peculiar advantages for study, and their flocculation phenomena are worthy of further investigation.

Note on Phosphatic Compounds

Comber's discovery that certain phosphatic materials exhibit anomalous flocculation in aqueous suspension, indicates that phosphates may exist as colloidal electrolytes, and may perhaps be amphoteric. The researches of Bassett[2] demonstrate that rock phosphate and bone consist mainly of either true compounds or adsorption complexes of tricalcium phosphate, calcium hydroxide and water. The water, at least, appears to be adsorbed, and this suggests that the phosphatic compounds may be of the hydrous oxide type, although some other relationship may account for their peculiar properties. Meig's observation that calcium phosphate can form a semi-permeable membrane, is ascribed to its hydrated colloidal nature[3].

Phosphates present peculiar features as components of soil and as soil amendments. They appear to be particularly strongly adsorbed, and to occur in a state of low availability in soils of lateritic type[4]. This is probably due to the formation of insoluble complexes between phosphate-ion (whether crystalloidal or colloidal), and the cations of hydrous alumina and ferric oxide, under suitable conditions of acidity. The recent researches of Gordon and Starkey[5], who found that colloidal alumina and ferric oxide possess a very much greater adsorptive power than colloidal silica for phosphate, furnish direct evidence of this. In many instances, the beneficial effect of phosphatic manures may actually be due to their flocculating action on those colloids, and may be of considerable significance in the amelioration of tropical laterites[1].

---

[1] Splichal: Chem. Abs. **15**, 3012 (1921); Smith: J. Am. Chem. Soc. **42**, 460 (1920).

[2] J. Chem. Soc. **111**, 620 (1917).

[3] Am. J. Physiol. **38**, 465 (1915).

[4] McGeorge: Agr. Exp. Sta. Hawaii, Bull. No. 41 (1916).

[5] Soil Science, **14**, 1, 449 (1922); Lichtenwalner, Flenner and Gordon: **16**, 157 (1923).

Summary

1. The flocculation phenomena of lateritic clays and soils are discussed on the basis of Comber's theory, which ascribes the anomalous flocculation of clay by lime to the formation of insoluble colloidal complexes.

2. Reasons are presented in support of the view that hydrous alumina and hydrous ferric oxide, which probably occur in laterites, are colloidal ampholytes, possessing isoelectric points not far removed from neutrality. On this assumption, the mechanism of their anomalous flocculation by lime, and by certain anions, such as silicate-ion and phosphate-ion, may satisfactorily be explained.

3. An attempt is made to extend the theory so as to embrace hydrous silica and hydrous aluminosilicates and hydrous ferrosilicates, and it is submitted that these colloids also may be regarded as ampholytes.

4. Mutual precipitation of colloidal ions is discussed in its relation to flocculation in certain soils.

The writer wishes to express indebtedness to his colleague, Mr. P. E. Turner, for many helpful suggestions.

Imperial College of Tropical Agriculture
Trinidad, B. W. I
December 24, 1924.

---

[1] Howard and Howard: J. Agr. India, **18** II, 148 (1923); Iyengar: J. Mysore Agr. Exp. Union, Bangalore, **4**, No. 3 (1923).

THE ULTRAVIOLET ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF SULPHUR DIOXIDE AND SOME OF ITS DERIVATIVES

BY FREDERICK H. GETMAN

In a paper treating of the relation between the absorption spectra of acids and their salts, Wright[1] was the first to direct attention to the fact that aqueous solutions of sulphur dioxide exhibit a well-defined absorption band in the neighborhood of $\lambda = 276\,\mu\mu$. Notwithstanding the marked absorption shown by solutions of sulphurous acid, the neutral salt, Na_2SO_3, was found to be diactinic. In commenting on this fact, Wright suggested that, in view of the doubtful constitution of sulphurous acid, further investigation of the behavior of these substances toward ultraviolet radiation would doubtless prove of interest.

At the time of publication of Wright's paper, the subject of the ultraviolet absorption of solutions of sulphur dioxide and various sulphites was being studied by Garrett[2] and also by Schaeffer, Niggemann and Koehler[3]. Garrett measured the extinction coefficients of H_2SO_3, $RbHSO_3$, $KHSO_3$, $NaHSO_3$, $(NH_4)_2SO_3$, $K_2S_2O_5$, $Na_2S_2O_5$, $CH_3 \cdot C(OH)\,(SO_3Na) \cdot CH_3$, $NaKSO_3$, Na_2SO_3, $C_2H_5 \cdot SO_2 \cdot O \cdot C_2H_5$, and $SO(OC_2H_5)_2$, employing a large Hilger quartz spectrograph in conjunction with a rotating sector photometer. The extinction curve for the acid was well-defined and easily reproducible, whereas with the acid sulphites the absorption was found to increase with time, attaining a maximum value in four or five weeks. This behavior was ascribed to the influence of light, since freshly prepared solutions, and solutions which had been kept in the dark, failed to show selective absorption. Metabisulphites were found to behave similarly to the acid sulphites. The normal sulphites of sodium and potassium, as well as the mixed sulphites of these metals, the symmetrical and unsymmetrical diethyl sulphites and acetone sodium hydrogen sulphite failed to exhibit selective absorption. From these facts the author decided that no conclusive evidence as to the constitution of the sulphites can be derived from the study of their absorption spectra. He attributed the absorbing power of sulphurous acid to hydrated sulphur dioxide, $SO_2 . nH_2O$, where *n* is indeterminate. Garrett summarized his conclusions by means of the following equations:—

(1) $Na_2S_2O_5 + H_2O = 2NaHSO_3$, (reaction in solution)

(2) $NaHSO_3 + NaHSO_3 = Na_2SO_3 + H_2SO_3$, (light reaction)

(3) $H_2SO_3 = SO_2 \cdot nH_2O$, (reaction in solution)

The relative amounts of hydrated sulphur dioxide present in equally concentrated solutions of the various acid sulphites were calculated and these quantities were shown to increase with increasing strength of the base, or, in other words, the equilibrium represented by equation (2) shifts toward the right as the strength of the base increases.

---

[1] Wright: J. Chem. Soc., **105**, 669 (1914).

[2] Garrett: J. Chem. Soc., **107**, 1324 (1915).

[3] Schaeffer, Niggemann and Koehler: Z. Elektrochem., **21**, 181 (1915).

Schaeffer and his associates studied the ultraviolet absorption of sulphur dioxide, sulphurous acid and several salts and esters of the latter by means of the familiar Hartley-Baly method. A comparison of the spectrum of a solution of sulphur dioxide in water with that of sodium sulphite indicated that the equilibrium in the reaction, $SO_2 + H_2O \rightleftarrows H_2SO_3$, lies toward the left side of the equation. On neutralizing a solution of sulphur dioxide with sodium hydroxide, the character of the spectrum was found to change from selective to total absorption in the ultraviolet. An excess of sodium hydroxide was found to exert little or no effect on the degree of absorption, which fact led the authors to conclude that sodium sulphite and its ions possess the same absorptive properties. Sodium bisulphite, prepared by adding the theoretical amount of sodium hydroxide to sulphurous acid, was found to exhibit a weak absorption in the ultraviolet resembling that of sulphurous acid. On the other hand, when sodium bisulphite was prepared by adding the correct quantity of sulphuric acid to the normal sulphite, an entirely different absorption spectrum was obtained which, after the lapse of twenty-four hours, became identical with the spectrum observed with bisulphite prepared by the former method.

Solutions of potassium metabisulphite, when freshly prepared, were found to give stronger absorption than sulphurous acid, but after forty-eight hours, the two spectra became identical.

In a later communication, Schaeffer and Koehler[1], continuing their studies on the ultraviolet absorption of aqueous solutions of sulphur dioxide, arrived at the conclusion that the true absorbent in solutions of sulphurous acid is a hydrate of sulphur dioxide which appears to be more active than sulphur dioxide alone. Since the normal sulphites and the esters, $C_2H_5 \cdot SO_2 \cdot O \cdot C_2H_5$ and $SO(OC_2H_5)_2$, are both diactinic, it is inferred that sulphurous acid *per se* is non-absorbing both in the ionized and unionized condition.

The diminution in the absorbing power of solutions of sulphur dioxide on dilution is traced to a shift from right to left in the equilibrium represented by the equation, $SO_2 \cdot H_2O \rightleftarrows H_2SO_3$.

Normal sulphites were found to show only end absorption in the extreme ultraviolet and when a solution of a normal sulphite was half-neutralized with sulphuric acid, the resulting acid sulphite at first showed only end absorption and then, after a few days, particularly under the influence of light, the band characteristic of sulphur dioxide was observed to develop. On the other hand, when the acid sulphite was formed by mixing solutions of sulphur dioxide and the normal sulphites, the band manifested itself immediately. A solution of potassium metabisulphite, when freshly prepared, was found to exhibit end absorption only, but on standing an absorption band gradually developed. In like manner, sodium methyl sulphite, which in alcoholic solution showed only end absorption, in aqueous solution gradually developed the sulphur dioxide band due to hydrolysis into sodium bisulphite and methyl alcohol. Schaeffer and Koehler summarize their views as to the equilibrium conditions in aqueous solutions of sulphur dioxide by the following equations:—

---

[1] Schaeffer and Koehler: Z. anorg. Chem., **104**, 212 (1918).

(1) $SO_2 \rightleftharpoons SO_2, H_2O \rightleftharpoons (O_2S \cdot OH)H \rightleftharpoons (O_2S \cdot OH)^- + H^+$

(2) $(O_2S \cdot OH)^- \rightleftharpoons (OS \cdot O \cdot OH)^- \rightleftharpoons (OS \cdot O_2)^- H \rightleftharpoons (OS \cdot O_2)^{=} + H^+$

They regard the ion, HSO_3^-, as unstable and tending to undergo transformation into H_2SO_3 and $SO_3^{=}$, as represented by the equation,

$$2H\,SO_3^- = SO_3^{=} + H_2SO_3.$$

The resulting sulphurous acid is then assumed to come into equilibrium with hydrated sulphur dioxide, as indicated by the equation,

$$H_2SO_3 \rightleftharpoons SO_2, H_2O.$$

In this manner, the authors account for the gradual development of the absorption band in solutions of sulphurous acid. The view is also expressed that the ion, $SO_3^{=}$, has a symmetrical structure and that this structure also obtains in the normal sulphites.

The equilibria of solutions of the alkali metal bisulphites was also made the subject of special investigation by Baly and Bailey[1] in connection with a study of the additive compounds formed by sodium and potassium bisulphites with aldehydes. These authors concluded that in aqueous solutions of bisulphites there is present in the equilibrium mixture a small proportion of metabisulphite which absorbs light of wave-length $\lambda = 257\mu\mu$. In the absence of oxygen, the solutions were found to be stable in light, but if oxygen or air is present, photo-oxidation of the HSO_3 ion occurs, followed by an ionic rearrangement in which normal sulphate, sulphurous acid and hydrated sulphur dioxide are formed. The solution was then found to show the band at $\lambda = 276\mu\mu$, characteristic of hydrated sulphur dioxide. The absorption bands of sulphurous acid, bisulphite and sulphite molecules were shown to lie in the extreme ultraviolet. It was furthermore pointed out, that the characteristic ultraviolet frequencies of sulphur dioxide, hydrated sulphur dioxide and potassium metabisulphite are integral multiples of the fundamental molecular frequency of sulphur dioxide in the infrared. No evidence was found for the existence of isomerism amongst the sulphite molecules.

While all the foregoing investigators are agreed that solutions of sulphur dioxide show a characteristic absorption band at $\lambda = 276\mu\mu$ and that solutions of bisulphites, on standing in the presence of oxygen, gradually develop a band at $\lambda = 276\mu\mu$, their statements relative to solutions of metabisulphites are conflicting.

Thus, Garrett, referring to the gradual development of a band at $\lambda = 276\mu\mu$ in solutions of bisulphites, states that this might be attributed to the formation of metabisulphite according to the equation,

$$NaHSO_3 + NaHSO_3 \rightleftharpoons Na_2S_2O_5 + H_2O.$$

If this be correct, then, quoting from Garrett's paper, "freshly dissolved metabisulphite ought to exhibit strong selective absorption from the moment of solution. It was found, however, not to be the case. Both sodium and potassium metabisulphite solutions behaved exactly similarly to the hydrogen sulphite solutions, and, in fact, reached the same constant maxima which those solutions had given." Schaeffer and Koehler, on the other hand, found that freshly prepared solutions of potassium metabisulphite exhibited end absorption only, but that on standing a band gradually developed. Baly and Bailey state, that freshly prepared solutions of potassium metabisulphite exhibit a characteristic absorption band at $\lambda = 257\mu\mu$ and that a similar band was observed in freshly prepared solutions of the alkali metal bisulphites. On exposure to light the band at $\lambda = 257\mu\mu$ disappeared and in its place a new band at $\lambda = 276\mu\mu$ gradually developed with marked increase in the absorptive power of the solution.

---

[1] Baly and Bailey: J. Chem. Soc., 121, 1813 (1922).

Again, it is by no means clear whether the progressive change undergone by solutions of bisulphites on standing is due to the action of light in the presence of oxygen, or to the action of light alone. With a view to clearing up these uncertainties the following investigation was undertaken.

Preparation of Materials. In preparing the solutions used in these experiments, due regard was had for the importance of purity of both solutes and solvents in spectrographic work. The sulphur dioxide solutions were prepared with gas obtained by the action of sulphuric acid on chemically pure, crystalline sodium sulphite. The evolved gas was dissolved in distilled water which had just previously been boiled to exclude air and carbon dioxide, precautions being taken to protect the solutions from oxidation after preparation. The solutions of sodium sulphite and bisulphite were prepared in a similar manner from chemically pure salts. Garrett states that he experienced difficulty in obtaining pure samples of sodium and potassium bisulphites and ultimately was forced to prepare the salts by passing sulphur dioxide into dilute solutions of the carbonates. It should be stated that the samples of sodium bisulphite used in this series of experiments were obtained from a well-known chemical manufacturer and upon analysis were found to correspond accurately with the formula of the salt. Considerable difficulty was experienced, however, in obtaining a satisfactory preparation of sodium metabisulphite. After examining several samples of this salt, obtained from different sources, and finding them all more or less impure, the attempt was made to prepare the salt by passing pure, dry sulphur dioxide into a solution of sodium ethylate in absolute ethyl alcohol. While a beautiful crystalline product was obtained, it was found upon analysis to be no purer than the commercial preparations previously examined. Ultimately, an excellent preparation of the potassium salt was obtained from a reliable chemical firm which, upon analysis, was found to conform very closely to the formula, $K_2S_2O_5$.

The concentration of the solutions was determined in each case by means of the familiar iodine-thiosulphate method.

Apparatus. The extinction coefficients of the various solutions studied were determined by means of a large size Hilger quartz spectrograph in conjunction with a Judd Lewis ultraviolet sector-photometer, as described by the author in a previous paper[1].

Experimental Data. The experimental results are expressed graphically by means of curves in which logarithms of molecular extinction coefficients are plotted against corresponding wave-lengths expressed in millimicrons, $\mu\mu$. The molecular extinction coefficient is defined by the expression $\frac{\log \frac{I_0}{I}}{ml}$

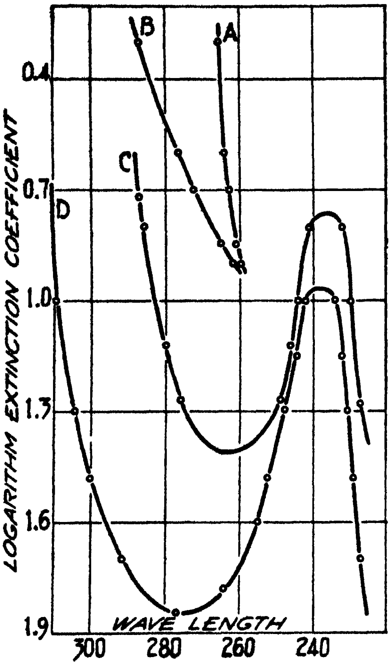


Fig. 1

A 0.05 m Sodium Sulphite
B. 0.05 m Sodium Bisulphite
C 0.02 m Potassium Metabisulphite
D 0.005 m Sulphur Dioxide

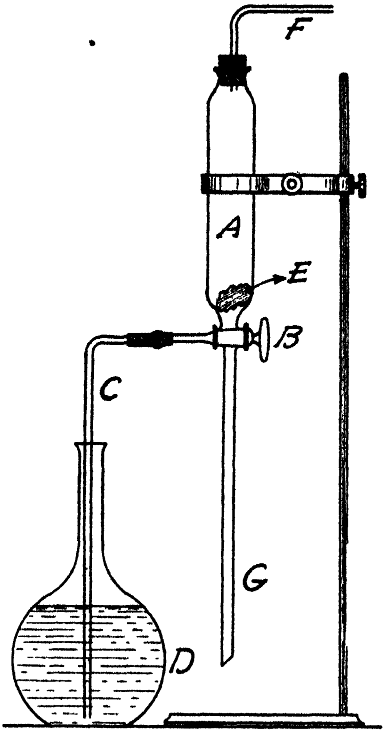


Fig. 2

where I_0 and I are the intensities of the incident and transmitted radiation respectively, and where m denotes the concentration of the solution in gram-molecules per liter and l is the length of the column of absorbing medium in cms.

The extinction curve of 0.05 m Na_2SO_3 is designated by the letter A in Fig. 1: The position of the absorption band is evidently in the extreme ultraviolet, as was pointed out by Baly and Bailey. Curve B is the extinction curve of freshly prepared 0.05 m $NaHSO_3$ and, as with the normal salt, the absorption band is found to lie in the extreme ultraviolet. The extinction curve of freshly prepared 0.02 m $K_2S_2O_5$ is represented by C. Special precautions were taken in the preparation of the latter solution to eliminate both air and carbon dioxide. To this end the apparatus shown in Fig. 2 was employed. A dropping funnel, A, of approximately 70 cc. capacity and fitted with a three-way stopcock, B, was connected through C with a flask, D, containing a large volume of freshly boiled, distilled water. A large clear crystal of potassium metabisulphite, E, was introduced into the funnel, the neck of which was then closed by means of a rubber stopper fitted with a right-angled tube F. The latter was connected with a water pump and B was turned so as to establish communication with the solvent in D. When sufficient water had been aspirated through the funnel to dissolve the surface layer of E and to insure the removal of the resulting solution, the stop-cock was closed and the crystal permitted to dissolve. When the bulk of the crystal had diminished to about that required for a solution of suitable concentration for use in the spectrophotometer, the supernatant solution in A was removed by further aspiration and the crystalline residue allowed to dissolve. Connection with the pump was then broken and, after allowing enough of the solution to flow out of the funnel to displace the air in G, the absorption cell was filled and the absorption spectrum immediately photographed. Another portion of the solution was analyzed simultaneously in order to determine its concentration. It will be observed that the solution gives a well-defined absorption band at $\lambda = 263\mu\mu$. The position of the head of this band was checked by repeated experiments. Curve D, Fig. 1, is the extinction curve of freshly prepared 0.005 m SO_2. The position of the head of the absorption band at $\lambda = 276\mu\mu$ is in agreement with the results of Baly, Garrett

---

[1] Getman: J. Phys. Chem., 29, 853 (1925).

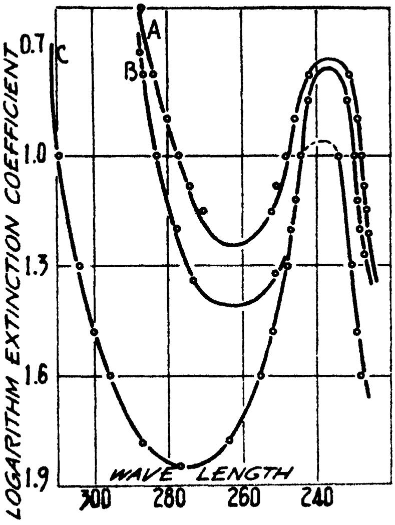


FIG. 3

A 0.025 m Potassium Metabisulphite
B 0.020 m Potassium Metabisulphite
C 0.005 m Sulphur Dioxide

and others. If due precautions were taken to exclude air and carbon dioxide, the curve for dissolved SO_2 could be satisfactorily reproduced. On repeating the experiment with solutions of different concentrations, it was found that Beer's law does not apply to aqueous solutions of sulphur dioxide. This is in agreement with the observations of Garrett.

Further experiments with potassium metabisulphite are summarized in Fig. 3. Curve A represents the results of two series of measurements of the extinction coefficients of 0.025 m $K_2S_2O_5$. Curve B, which is a reproduction of curve C of Fig. 1, serves to illustrate the inapplicability of Beer's law to aqueous solutions of metabisulphites. Although the foregoing experiments confirm the statement of Baly and Bailey, that solutions of metabisulphites give a characteristic absorption band, we have been unable to check their result as to the location of the band. They state that the wave-length corresponding to the head of the band is $\lambda = 257\mu\mu$, whereas we find $\lambda = 263\mu\mu$. Since potassium metabisulphite rapidly decomposes in solution with the formation of sulphur dioxide, it follows that its solutions on standing will develop the band characteristic of dissolved sulphur dioxide at $\lambda = 276\mu\mu$.

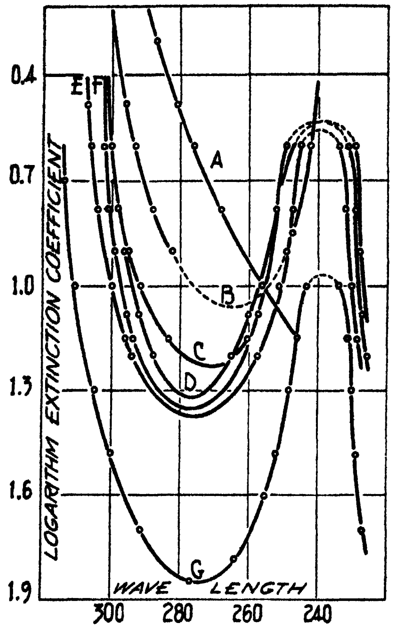


Fig. 4

A	0.05 m	Sodium Bisulphite	(freshly prepared)
B	0.05 m	” ”	(after 18 hours)
C	0.025 m	” ”	(after 5 days)
D	0.025 m	” ”	(after 10 days)
E	0.025 m	” ”	(after 20 days)
F	0.025 m	” ”	+ 0.02 m Sucrose (after 30 days)
G	0.005 m	Sulphur Dioxide	

The results of the measurements of the extinction coefficients of solutions of sodium bisulphite are brought together in Fig. 4. Curve A was obtained with freshly prepared 0.05 m $NaHSO_3$. After 18 hours the extinction curve of this same solution was found to have changed to that represented by curve B. As will be seen, the character of the absorption has changed from general or end absorption to selective absorption. In order to follow more closely the progressive change in the composition of solutions of sodium bisulphite with time, a large volume of 0.025 m $NaHSO_3$ was prepared, taking the usual precautions to exclude air and carbon dioxide. With this mother solution, five series of experiments were carried out. In the first series, approximately 100 cc. portions of the mother solution were introduced into flasks of 125 cc. capacity and, after stoppering, the flasks were exposed to light for varying periods of time. In the second series, a number of 50 cc. bottles fitted with ground stoppers were completely filled with the mother solution. After inserting the stoppers, the necks of the bottles were sealed with paraffine and, as in the case of the preceding series, exposed to light for varying periods of time.

The third series resembled the first series in every particular except that to the original solution enough cane sugar was added to make the solution 0.02 molar with respect to that solute.

The fourth series was similar ot the second, except that the composition of solution was 0.025 m $NaHSO_3$ + 0.02 m $C_{12}H_{22}O_{11}$. The last series consisted of partially filled flasks of 0.025 m $NaHSO_3$ which were protected from the action of light. The progressive change in the composition of the solutions was determined both spectroscopically and analytically by examination of the contents of the different flasks and bottles at intervals of from five to ten days. The analytical procedure consisted in titrating the solutions against 10 cc. portions of N/10 iodine to which a few drops of hydrochloric acid had been added to insure complete liberation of combined sulphur dioxide. The results of the analytical examination are given in Table I.

TABLE I

Initial titer, 10 cc. N/10 I = 9.6 cc. $NaHSO_3$

Interval (Days)	Titer I	II	III	IV	V
5	....	9.6	....	9.6	....
10	12.9	9.5	....	9.5	....
15	....	...	....	...	9.9
20	27.0	9.6	24.5	9.8	....
30	62.7	9.7	31.8	9.7	10.2
50	....	...	....	...	10.7

As will be seen from columns II and IV of the table, the titer of the solutions from which air had been excluded remains constant, whereas the figures in columns I and III increase, indicating gradual oxidation of the solution. That light plays an important part in the process of oxidation is indicated by the figures of the fifth column. It will be remembered that although this solution was in contact with air it was placed in the dark immediately after preparation. After a period of two months the solution had not oxidized as much as the same solution had oxidized in ten days under the influence of light. It has been shown by Mathews and Weeks[1] that cane sugar and a number of other organic compounds act as negative catalysts in the oxidation of solutions of sodium sulphite. That a similar action is exerted by cane sugar when dissolved in a solution of sodium bisulphite is revealed by a comparison of the data of I and III columns of the table. Cane sugar was selected from the list of catalysts enumerated by Mathews and Weeks because it was believed that its presence in a solution of sodium bisulphite would produce little or no alteration in the characteristic absorption spectrum of the salt.

The progressive change in the absorption of 0.025 m $NaHSO_3$ is depicted by the curves of Fig. 4. It is apparent that after standing for ten days the head of the absorption band becomes constant at $\lambda = 276\mu\mu$, the wave-length characteristic of dissolved sulphur dioxide. The retarding action of cane sugar on the process of oxidation is clearly shown by the fact that 0.025 m $NaHSO_3$ twenty days after preparation has greater absorbing power than the same solution containing 0.02 gram-molecule of cane sugar thirty days after preparation (curves E and F).

Discussion of Results. In reviewing the foregoing experimental data it is apparent that aqueous solutions of sodium bisulphite are stable in light provided oxygen is excluded, but if oxygen or air is present, photo-oxidation ensues and, after five days, the solution shows the characteristic absorption band of dissolved sulphur dioxide at $\lambda = 276\mu\mu$. Since the absorption curve of 0.025 m $NaHSO_3$, five days after preparation, corresponds very closely with that of a mixture of equal volumes of 0.05 m SO_2 and 0.05 m Na_2SO_4, it may be fairly assumed that the progressive change in the solution under the influence of light consists in the photo-oxidation of the anion of sulphurous acid, HSO_3^-. The successive steps in the process may be represented by the equations:—

$$NaHSO_3 \rightleftarrows Na^+ + HSO_3^-, \tag{1}$$

$$Na^+ + HSO_3^- \xrightarrow[\text{light}]{(O)} Na^+ + HSO_4^-, \tag{2}$$

$$Na^+ + HSO_4^- \longrightarrow Na^+ + H^+ + SO_4^=, \tag{3}$$

The resulting ions then react with the ions of (1) in the following manner:—

$$Na^+ + H^+ + SO_4^= + Na^+ + HSO_3^- \longrightarrow 2Na^+ + SO_4^= + H^+ + HSO_3^-, \tag{4}$$

$$H^+ + HSO_3^- \rightleftarrows H_2SO_3 \rightleftarrows SO_2, H_2O. \tag{5}$$

Freshly prepared solutions of potassium metabisulphite have been found to give a well-defined absorption band at $\lambda = 263\mu\mu$, provided precautions are taken to exclude air and carbon dioxide. This fact proves that, initially, solutions of metabisulphites and bisulphites are not identical, as has been claimed by several investigators. Solutions of metabisulphites rapidly hydrolyze as indicated by the equilibrium equation,

$$K_2S_2O_5 + H_2O \rightleftarrows 2KHSO_3, \tag{6}$$

---

[1] Mathews and Weeks: J. Am. Chem. Soc., 39, 635 (1917).

and the resulting bisulphite then undergoes photo-oxidation, as indicated in the preceding paragraphs.

No indication of the existence of a band at $\lambda = 257\mu\mu$, in freshly prepared solutions of sodium bisulphite, as claimed by Baly and Bailey, was obtained, but the fact that they prepared their solutions of sodium bisulphite by half-neutralization of sulphurous acid with sodium hydroxide, whereas a pure dry salt was used in the present investigation may easily account for this discrepancy. In this connection it may be mentioned that although Garrett took extreme care in the preparation of his solutions he failed to record the existence of any band at $\lambda = 257\mu\mu$ in solutions of the bisulphites. Baly and Bailey estimate that in 0.025 m $NaHSO_3$ there is probably less than three percent metabisulphite, indicating that the equilibrium in reaction (6) lies toward the right side of the equation.

Baly and Bailey apply to the two absorption bands observed by them at $\lambda = 257\mu\mu$ and $\lambda = 276\ \mu\mu$, a relationship previously established by the senior author[1]. By means of a mathematical deduction from the quantum theory, Baly showed that if ν_x is the wave-number of the characteristic infra-red vibration of a compound, then radiant energy can only be reabsorbed at the wave-numbers ν_1, ν_2, ν_3, etc., where ν_1, ν_2, ν_3, are successive integral multiples of ν_x. In the present example, SO_2 is the absorbing molecule and this has been found to exhibit a characteristic absorption band corresponding to each of the three following states:—(a) gaseous SO_2, (b) $SO_2.H_2O$, and (c) $K_2SO_3.SO_2$. As Baly and Bailey have shown, the fundamental wave-number of gaseous SO_2 is 135.1 and therefore, according to the above generalization, the wave-numbers of the three bands should be integral multiples of this fundamental quantity. The following table is taken from their paper.

TABLE II

Multiple	$1/\lambda$	λ (calc)	λ (obs.)	Origin of band
25 × 135.1	3377.5	$296.1\mu\mu$	$296.1\mu\mu$	SO_2
27 × 135.1	3647.7	274.1	276.0	$SO_2 \cdot H_2O$
29 × 135.1	3917.9	255.2	257.0	$K_2SO_3 \cdot SO_2$

If the fundamental wave-number of SO_2, 135.1, be multiplied by 28 instead of 29, as in the table, the calculated value of the wave-length of potassium metabisulphite becomes $\lambda = 264.3\mu\mu$, which is in quite as good agreement with our observed value, $\lambda = 263.0\mu\mu$, as is Baly and Bailey's calculated with their observed value.

Summary of Results. The results of the foregoing investigation may be briefly summarized as follows:—

(1) Aqueous solutions of sulphur dioxide show a characteristic absorption band at $\lambda = 276\mu\mu$. The absorption is attributed to hydrated sulphur dioxide, $SO_2.H_2O$, formed from the anion of sulphurous acid. The extinction curve for sulphur dioxide solutions of the same concentration is easily re-

---

[1] Baly: Phil. Mag. (6) **27**, 632 (1914); **29**, 223 (1914); **30**, 510 (1915).

producible, provided oxygen and carbon dioxide are excluded. Beer's law does not apply to aqueous solutions of sulphur dioxide nor to any of its derivatives.

(2) Freshly prepared solutions of potassium metabisulphite give a characteristic absorption band at $\lambda = 263\mu\mu$. On standing, this band disappears and in its place the sulphur dioxide band at $\lambda = 276\mu\mu$, gradually develops. The fact that metabisulphite solutions give a well-defined band at $\lambda = 263\mu\mu$, is taken as evidence of the existence of the undecomposed salt in solution.

(3) Solutions of sodium sulphite do not show selective absorption.

(4) Freshly prepared solutions of sodium bisulphite show end absorption only, but on standing in the light, if oxygen is present, photo-oxidation of the ion, HSO_3^-, occurs with the simultaneous development of the band at $\lambda = 276\mu\mu$ characteristic of dissolved sulphur dioxide. The magnitude of the absorption coefficient continues to increase for about thirty days when a constant maximum is attained.

(5) The presence of cane sugar in solutions of sodium bisulphite has been shown to retard the process of oxidation.

(6) Light has been found to be an essential factor in the oxidation of bisulphite solutions.

(7) Baly's relationship connecting ultraviolet frequencies with a fundamental frequency in the infra-red has been found to be applicable to the bands at $\lambda = 263\mu\mu$ and $\lambda = 276\mu\mu$, characteristic of $K_2S_2O_5$ and $SO_2.H_2O$ respectively.

Hillside Laboratory,
Stamford, Conn.

ORIGIN OF THE FORMATION OF DEPOSITS IN GOUT AND OTHER DISEASES AND THE CAUSE OF SWELLING IN BERIBERI

BY N. R. DHAR

Gout has been defined "as a disorder of metabolism associated with retention of uric acid, and of other purin bodies in the system, characterised clinically by attacks of acute arthritis, the deposition of sodium biurate in and about the joints and by the occurrence of irregular constitutional symptoms"[1]

The veins around the painful joint first appear swollen and shortly the whole joint becomes swollen, tense, shining and of a deep red colour. The subcutaneous tissues are oedematous and pit on pressure.

An attack of acute gout is commonly preceded by some troubles of digestion—acidity, flatulence, loss of appetite, constipation, and scanty, high coloured urine. Before and at the commencement of the attack the output of uric acid is generally low, but rises to normal or above with full establishment of the arthritis. There is a remarkable parallelism in the output of uric and phosphoric acids both during and between the attacks.

It is believed that these joint affections are dependent on the precipitation and deposit of sodium biurate crystals in the cartilages, ligaments, synovial membranes, bursae, and other structures forming part of, or in proximity to, the articulation. In some of the most distressing forms of chronic gout, the joints of the fingers, and less frequently those of the toes, become surrounded by massive deposits of sodium biurate which sometimes ulcerate slowly through the skin. It has been observed that masses as large as horse beans are discharged.

Small deposits of sodium urate are also often observed on the margins of the ears and occasionally on the insides of eyelids, on the arches of the pallets and elsewhere. The most serious manifestations of gout are the cardiovascular and renal changes that are determined by the gout state.

The crystalline urates precipitated in the cartilaginous and fibrous structures of the joints necessarily act as foreign bodies. They excite irritation, clog the lymph channels, exercise pressure on the tissue elements and impede their nutritive operations; hence the inflammation, pain, swelling and subsequent regenerative changes in the joints.

According to newer views gout is regarded as the disturbance of purin metabolism, or a perversion of the general metabolism of the tissues. It is believed then that uric acid plays only a secondary part in the causation of gout and is a mere weapon of the disease. That its excess in the blood is probably due to diminished oxidation in the system; that somewhere in the body a ferment is produced which normally is necessary for the proper oxidation of uric acid, and that owing to some organ or organs failing to produce this ferment, proper oxidation of uric acid does not occur, and it consequently accumulates in the blood. It is certain that an excess of uric acid in the blood cannot alone be regarded as the cause of the deposition of sodium biurate or of uric acid in the tissues, for in leukaemia there is a notable increase of uric acid in the blood, yet it is not usual to find biurate or uric acid deposition in the tissues.

---

[1] Osler: "Principles and Practice of Medicine", 417 (1912).

Thus the modern tendency is to believe that ferments play an important part in the formation and destruction of uric acid in the blood. It is suggested that it is formed partly by oxidative processes from the nucleo-proteins, and partly by a synthetic process in the liver.

Gout is due to a disorder of elimination, a defect or feebleness in the function or functions of the elimination of the waste products of nutrition.

The value of alkalies in the treatment of gout has been almost universally accepted. "Alkalies" testifies, Professor Whitla[1] "by forming soluble salts with uric acid, which salts, acting as diuretics, are freely washed out in the urine, cause marked elimination of uric acid, and are the most valuable of the gouty remedies."

I am of the opinion that alkalies also help in the increase of metabolism in the system. We have repeatedly observed in the laboratories that the oxidation of carbohydrates by air at the ordinary temperature in presence of reducing agents like $Fe(OH)_2$, cerous hydroxide etc., is greatly increased by the increase in the concentration of the alkalies. It is now well known that acidity of the system is associated with disturbance of digestion and that acidosis is essentially connected with insufficient metabolism and is mainly responsible for the causation of gout.

From my researches on colloids, I am convinced that sparingly soluble substances like uric acid, calcium phosphate, calcium oxalate etc., remain in the colloidal condition in the system due to the presence of protecting albuminous substances. When these colloidal substances are coagulated and are crystallised in tissues we get diseases like gout, renal colic, oxaluria, lithiasis, phosphaturia, gallstones, etc., which are diseases caused by the deposition of the sparingly soluble substances in various parts of the body.

How this coagulation takes place? The coagulation of peptised substances can take place due to one or more of the following causes:—

1. Increment of electrolytes in the system.
2. Decrease of the peptising influence either by loss or dilution of the protecting agent.
3. Decrease of temperature.
4. Increase of concentration of the substance which is being peptised.
5. Adsorption of the peptised substance by some solid adsorbent.

We have proved definitely that substances like $BaSO_4$, freshly precipitated $Fe(OH)_3$, $PbCrO_4$, etc. can adsorb appreciable quantities of sols of various substances. Hence we are convinced that the bone or the cartilage of the system can surely adsorb the peptised uric acid, calcium oxalate calcium phosphate, etc. existing in the system; consequently the deposition of these substances is certainly very favourable round about the bones, cartilages and in joints. It is a well-established fact that the presence of solids favour the formation of a precipitate from a colloidal matter or from a solution.[1]

---

[1] Whitla: "Dictionary of Treatment", p. 376.

I have already emphasised that an attack of gout is commonly preceded by some troubles of digestion—acidity, constipation, scanty and high coloured urine, etc. I believe that when the system is not working in the proper condition and the excretions are not normal, we get an extra amount of water in the system and this water acts as a diluent of the protective agents and hence the amount of uric acid or calcium phosphate or calcium oxalate held in the colloidal condition is decreased due to the decrease in the concentration of the protective agents (albuminous substances) in the system caused by dilution.

I am of the opinion therefore that an important cause in the formation of the deposits of uric acid, calcium phosphate, calcium oxalate, etc. is the presence of an extra amount of water which in normal circumstances should have been eliminated from the system, but when a person is suffering from constipation, scanty urine, etc., the water does not come out of the system in normal quantities, but dilutes the peptising agent (albuminous matter) and hence substances like uric acid, calcium oxalate, calcium phosphate, etc., which normally remain in the peptised condition in the system become coagulated.

We have shown that the amount of silver chromate held in suspension by gelatin decreases with the decrease in the concentration of gelatin; similarly the amount of lead chromate or lead iodide remaining in the colloidal solution increases with the increase in the concentration of agar.[2]

Moreover in the case of gout the acidity which is usually associated with an attack of gout plays a very important part in the separation of uric acid. From the researches of Pauli and Samec we know that the solubility of sparingly soluble substances is increased by the presence of serum albumin and other protective agents, whilst the solubility of readily soluble substances are decreased due to the presence of albuminous substances. Bechhold and Ziegler have shown that the solubility of uric acid is much greater in serum albumin than in water, whilst that of sodium urate is decreased due to the presence of serum albumin. It seems certain that in gouty blood sodium urates should also be present along with uric acid. Now if the blood becomes acid due to insufficient oxidation and causation of acidosis, the sodium urate will be decomposed by the acids (lactic, phosphoric etc.) thus generated and uric acid will be set free, which, being more sparingly soluble than sodium urate is likely to come out as a precipitate due to the presence of the already existing urate ions. Consequently the acidity caused by the lack of proper metabolism helps in the precipitation of uric acid in gout.

---

[1] Compare Dhar and Chatterji: J. Phys. Chem. **28**, 41 (1924).

[2] Compare Sen and Dhar: Kolloid-Z. **34**, 270 (1924).

It is well known that the swelling of organic substances, like gelatin, albumin, etc., in water is greatly accelerated by the presence of small quantities of free acid or alkali; consequently the acidity produced in the system due to want of proper metabolism helps in the retention of water by the tissues and thus facilitates the dilution of the protecting agent (albuminous matter, etc.) and causes the separation of uric acid. Consequently our theory of the causation of gout, oxaluria, phosphaturia, renal colic, lithiasis etc., where deposits are formed in the system is exactly on the same line as that of Martin H. Fischer for the formation of oedema.

It will be interesting to note that practically the same treatment has been recommended by medical men in gout, oxaluria, renal colic, phosphaturia, lithiasis, gallstones, uninary calculi, oedema, etc., Alkalies like sodium bicarbonate, potassium bicarbonate, etc., have been recommended for the treatment of all these diseases. Alkalies help the oxidation of food stuffs in the body and hence they prevent the formation of acids and check acidosis. Moreover, they neutralise the acids already formed and consequently fight the above diseases. Flushing of the system with large quantities of water has also been recommended; this certainly causes the solution or mechanical carrying away of the precipitates by large volumes of water.

Purgatives have been found to be effective in the treatment of gout and according to our theory they should be effective, because they help the elimination of large quantities of water, purin bodies, etc.

It is well known that gout is prevalent in cold and humid climates; this becomes clear from our point of view because loss of water by perspiration, evaporation, etc., is much less in humid and cold climates than in warm dry climates and hence the retention of water and consequent dilution of the protective agents in the system is facilitated in humid and cold climates. Moreover, decrease of temperature markedly decreases the amount of solids which a certain amount of protective agent can hold in suspension. We have repeatedly observed that the amount of lead iodide or lead chromate which a certain weight of agar can hold in suspension is much greater at higher temperatures than at ordinary temperatures. Hence a lowering of body temperature helps in the formation of a deposit of uric acid, calcium phosphate, calcium oxalate, etc.

We have observed that the addition of alcohol makes a sol say of Ag_2CrO_4 peptised by gelatin unstable towards electrolytes. Hence we believe that alcohol would help the coagulation and separation of uric acid crystals in the system and that is why alcohol has been generally recognised as bad for gout.

It will be interesting to discuss in this connection the etiology and causation of beri-beri. It is now well-known that want of vitamin B in food stuffs leads to the causation of beri-beri. I am of the opinion that vitamin B acts as an accelerator or promoter for the oxidation of carbohydrates by air in presence of enzymes. Consequently want of vitamin B would lead to insufficient metabolism and acidosis, and the presence of acids will help in the retention of water in the animal economy. It is well-known that in beriberi water is retained in various parts of the body and causes swelling. I am of the opinion, therefore, that the swelling in beri-beri is due to the presence of acids caused by the deficiency in metabolism or carbohydrates of foodstuffs and alkalies ought to be beneficial for patients suffering from beri-beri, and I should request medical men to treat beri-beri with food materials rich in vitamin B together with some alkali to neutralise the acid generated by insufficient metabolism. It is very interesting to note that beri-beri is most common in nations who have to depend mainly on foods rich in carbohydrates. This explanation of the swelling in beri-beri is on the same line as that of Martin Fischer for oedema.

Summary and Conclusion

1. Gout, oxaluria, renal colic, phosphaturia, gallstones, lithiasis, etc., are mainly due to insufficient metabolism and deficiency of elimination of waste products.

2. An important cause in the formation of the deposits of uric acid, calcium phosphate, calcium oxalate, etc., is the presence of an extra amount of water due to want of proper elimination and this water dilutes the peptising agents and thus leads to the deposition of the above substances.

3. Acids generated in the system due to insufficient oxidation plays an important part in the deposition of uric acid by the decomposition of urates and by helping in the retention of water by the tissues and the albuminous parts of the body and the water thus retained dilutes the peptising agents and causes the precipitation of uric acid, calcium oxalate, etc.,

4. I am of the opinion that uric acid and not urates forms the main deposit in gouts.

5. Beri-beri is most probably due to insufficient metabolism of carbohydrates in the system due to the want of vitamin B in food stuffs. The acids generated in the system due to insufficient oxidation helps in the retention of water and causes swelling of different parts of the body.

Chemical Laboratory,
Allahabad University,
Allahabad, India,
April 29, 1925.

NEW BOOKS

Chemistry in Modern Life. *By Svante Arrhenius. Translated by C. S. Leonard. 22 × 16 cm; pp. xvi+286. New York: D. Van Nostrand Company, 1925. Price: $3.00.* In the preface the author says: "The bitter experience given us by the World War, and by the after years of exigency, demonstrated with hard-fisted emphasis the necessity for chemical industry. So we see today how the nations are trying to develop this branch of science for the best possible improvement of their situation. The most practical way to repair the heavy losses caused by the war lies in the application of chemistry."

This is a popular book on chemistry and the chapters are entitled: ancient ideas about the constitution of matter; the ground-work of scientific chemistry; fire, oxidation, and reduction; tools and metals; the cultural value of silica; the chemistry of the earth's crust; ores and fossil fuels; the chemistry of water and air; sources of energy, electricity and chemistry the course of a chemical process; dyes, perfumes, and drugs; cellulose and rubber; chemistry and the bread question; housekeeping with the treasures of nature.

"It should be noted that Lavoisier had numerous predecessors who came near to a correct conception about combustion. We have mentioned the genius, Leonardo da Vinci (1452-1519). This man, who accomplished marvellous work in all the arts and sciences of his time, also suggested a theoretical explanation of the problem of combustion. According to Leonardo air was consumed in the process of burning, and animals could not live in an air which, after bodies had been burned therein no longer could support combustion. Thus Leonardo discovered the fact that air consisted of two parts, of which one, now called oxygen, could support combustion and was necessary for the respiration of animals, while the other, now called nitrogen lacked these properties," p. 24.

"A very remarkable statement has been found by Klaproth in a Chinese manuscript of the eighth century. The author, Mao Khoa, reported therein that air was composed of two constituents, yin and yang. Yin could be removed from the air by the use of divers metals, or by sulphur, or carbon;—it must therefore have been oxygen. Yin could also be prepared from a certain mineral, the name of which is given. Klaproth presumes that this word meant saltpeter, but is not sure of this.

"The Byzantines very probably knew of gunpowder in the seventh century, the Chinese surely in the tenth century. Saltpeter is a constituent of this. From China the use of gunpowder passed to Persia and Arabia, where saltpeter was called the Chinese salt, or Chinese snow. The Arabs probably taught the Europeans the art of handling gunpowder," p. 25.

"Flint lends itself to use for tools because of the sharpness of its edges. Flint is an amorphous, which is to say a noncrystalline, substance. Amorphous substances, of which glass is best known, are charactèrized by a shell-like, or scale-like, mode of fracture, and as a result of this the edges formed by the fracture are very sharp. That is why one can so easily cut oneself on bits of broken glass, while pieces of the coarsely crystalline rocks, such as granite, are not at all dangerous when broken. In primitive times men sometimes used a true glass, volcanic in origin, called obsidian, for making edged-tools, and because of the traditional age of such tools, the Jews, today, use knives of obsidian for religious purposes. Flint also possesses the necessary hardness for use as a tool. It is very widespread, too, in its occurrence in chalk-formations all over the world," p. 60.

"The making of pottery vessels has been of the greatest importance in the development of a sense of beauty in man, for undoubtedly clay objects were an incentive to the use of ornamentation. It was probably noted that the impressions from the fingers that resulted from working the clay were found to remain after firing and to be permanent. Next a pleasure was found in designing an ornament by applying such finger marks in a regular arrangement, see Fig. 15. Later it was preferred to make the marks needed for ornamentation of the clay by the use of pointed objects. A fine example of what could be made even in the stone age by means of this simple technique may be seen in Fig. 16, which is a picture, 1/6 size, of a clay urn found on the island of Moen in Denmark," p. 86.

"There is no question but that the art of fabricating glass arose in Egypt about 5000 years ago. Articles of glass were first brought into Greece by the mercantile and sea-going peoples such as the Phoenicians, who, like the Assyrians, early learned how to work glass. The Greeks are not known to have practiced the art before the days of our calendar. Thus the Egyptians and the Phoenicians were looked upon at that time as the great masters of glass technique, and Alexandria was world-renowned for the remarkable glass articles sold in its markets.

"In the Roman state glass manufacture was first taken up on a large scale in the days of the Caesars, and the products were marketed even in the far East. In China the art of glass manufacture was first learned about the middle of the fifth century A. D. In spite of the high reputation held by Roman glass it was rather highly colored, having a green or yellow tint, like the simplest kinds of glass of today, and moreover it was full of small blowholes and nodules. On this account it was generally colored deeply or made opaque by the addition of chemicals and was used mainly for decorative purposes, and for jewelry, such as the cameo, and also for mosaics, etc. Only in very isolated cases was it used for windows; such use may be seen in the excavations at Pompeii. In the first century A. D. glass began to be used to a greater and greater extent for church-windows, but this glass was not clear, and consisted of small colored bits, which transmitted only a mystic half-light. The manfacture of glass next passed over to Constantinople and the Mohammedan Orient. The art returned to Europe during the Middle Ages. Venice became its chief center. When the Renaissance came and progress began again, glass factories, like all else, were influenced by the general desire to find artistic expression and the glass-industry of Venice reached a very high point in the 16th and 17th centuries. From Italy the art spread to France, which country was destined next to take the leading place in this branch of human culture. Even in Germany, and especially in Bohemia at the same period a great glass industry began to develop. In the last half-century Germany has stood at the top in this field. More and more all cultural lands have attained high proficiency in the art," p. 96.

"From lime-glass which is long heated to a high temperature there separates long crystals of pseudo-wollastonite (calcium silicate). As a result the glass acquires a porcelain-like appearance. Such glass is named after Réaumur who first noted the property. Attempts have been made to use this glass as porcelain but it is found to be very brittle so that it has little use. Zinc oxide can be dissolved in glass to such an amount that, on cooling, it crystallizes out in long needles. These can be colored a green or blue color by adding nickel or cobalt, which enter into the zinc silicate crystals. This fact is made use of for the preparation of artistic glazes on porcelain. Aventurine glass is characterized by the presence of small red copper crystals embedded in the glass. It results from the presence in the glass of both copper silicate and ferrous oxide. The latter during a slow cooling of the glass is oxidized at the expense of the copper oxide out of the silicate, so that copper [?] precipitates in crystalline form," p. 105.

Arrhenius seems to be rather impressed by the work of Ross, p. 110. "The chemist, William Ross, at the University of Washington in Seattle, has investigated a process which appears to be most promising. He first tried to get potash from potash felspar by heating the rock with a steam at 500° C. and under the enormous pressure of 1450 atmospheres. This experiment was unsuccessful. Next he heated the felspar with lime in water at 300° under about 90 atmospheres of steam pressure. He then found that a large part of the potash had been displaced by the lime, and had dissolved in the water. When the lime was made double the amount of the felspar, practically all the potash was freed. He now added still more lime so that the mass remaining after leaching out the potash would have about the same composition as the mixture from which Portland cement is made. (Felspar is about 25% low in alumina in comparison with the silica content, but this seems to make little difference in the value of the product). He investigated the potash yield at different temperatures. It was found that at 2000° and 16 atmospheres pressure, 93% of the potash could be separated. At higher temperatures higher yields were possible, but it was convenient and more practical to work at the low temperature of 200°. So it should be comparatively simple to design an economically advantageous process along these lines, first removing the potash, then making cement from the remaining mass."

"Many rocks such as granites are buried under the surface of the earth and cannot therefore have given off their gas-content to the air. The gases are still locked up in the stone. If the stone is crushed and pulverized and the powder heated, the gases pass out. So much gas is occasionally present that the stone explodes when it is struck by a hammer. This is true of the red quartz from Branchville, Conn. Similarly granite from Monson, Mass., is let stand some time after quarrying, and little particles of stone often fly at high velocity from its surface as the gas pressure is relieved. The gas content of the Branchville rock is made up of 98% carbon dioxide, the rest nitrogen with a trace of other gases. Granites and gneiss give off gas amounting to 2.5 to 7 times and even up to 18 times their own volume, measured at 18° C. and atmospheric pressure. These gases are mainly hydrogen and carbon dioxide with a little methane, carbon monoxide, nitrogen, and hydrogen sulphide. Water is not generally present, though at times it may be the chief constituent. Gautier calculated that a cubic centimeter of a granite which he investigated gave off 20 liters of gases when heated to 1000° C., and 80 liters of water measured at 1000° and atmospheric pressure. Very often the vapors from volcanoes attack rock masses lying nearby, setting free carbon dioxide from the limestone, and hydrogen sulphide from sulphur compounds," p. 113.

"The flakes of lime that are precipitated by organisms contain a little magnesium, and on the average this amount is one per cent. Many algae remove even more magnesium carbonate, in some cases up to thirteen per cent (according to Högbom). From such material magnesia-limestones are formed. Högbom has further shown that when such rock is weathered by carbonated water, lime dissolves out faster than does magnesium and so the residue approaches nearer and nearer in composition to dolomite, $MgCa(CO_3)_2$. Also water containing magnesium salts in solution can wash calcium carbonate out of limestones and replace it with magnesium carbonate. Dolomite, and dolomite limestones are widely distributed rock material.

"These rocks often contain iron, partly due to the action of plants, which may cause iron carbonate to be precipitated along with the lime and magnesia. Iron carbonate can replace calcium carbonate just as can the magnesium salt when solutions containing iron come into contact with limestones. In this way large areas of iron-spar or siderite (iron carbonate) are formed. In the presence of water containing oxygen this mineral easily changes to limonite (iron hydrate) and this, by the action of heat and pressure, to hematite, Fe_2O_3, or to magnetite, Fe_3O_4. The remarkable, huge, iron deposits around Lake Superior are believed to have been formed in this way from original deposits of siderite," p. 122.

"If a radium preparation is preserved in a glass vessel this glass becomes colored a dark violet color. When the glass is heated the color disappears. This coloration results from the action of the radiation from the radium, and it develops more rapidly the more rays the preparation sends out. It has been known for a long time that many minerals such as tourmaline and mica display under the microscope dark spots in their layers, which are called 'pleochroic halos,' (places which under polarized light show various colors). Joly in 1907 discovered that these dark places were due to radiations from little, enclosed kernels of radioactive material, containing uranium. From measurements of the size and the uranium content as well as by intensity of the color of these spots, it was determined that these preparations which came from rock of the Devonian period had an age of about 400 million years," p. 124.

"Concern about our raw materials casts its dark shadow over mankind. Those states which lack throw lustful glances at their neighbors, which happen to have more than they use. Still more tempting is the desire for gain from lands on the other side of the seas, inhabited by uncivilized natives, with interest unawakened to guardianship. Historical research of the future will demonstrate how much desire for raw materials was a cause of the recent great misfortune whose effects mankind, or better, the so-called civilized nations, are still undergoing. It is clear that some day we must come to forbid national egotism, equally with the profit-seeking of industries, from seeking a solution of the problem of the proper use of raw materials. Mankind must finally come to the viewpoint that in every possible way it will spare these raw materials for the future and that it will make use instead of the great power for work poured out by the sun above us in apparently undiminishing amount; or else will use the sun indirectly by employing the energy which is collected together in the form of water-flow, and in the green plants; for these are sources which can renew themselves," p. 143.

"Calcium carbonate precipitates from sea water partly as crystalline limestone, as one can see at the mouth of the Rhone river, or along the Florida coast, but by far the greater part is removed by organisms—corals, mollusks and pteropods. Their limy-shells and skeletons contain crystalline calcium carbonate. It is calculated that yearly 2300 million tons of chemical substances are precipitated in the ocean, of which the largest portion, about 1300 million tons consists of calcium carbonate, while of the remaining 1000 million about one-third is silica, which is removed by organisms. and the rest consists of about 280 million tons of magnesium carbonate, 60 million tons of potash, 75 million tons of iron oxide and various other related oxides, and a residue of sulphate, which for the most part becomes reduced to metallic sulphides. The carbon dioxide content of sea water varies with the depth. At the surface it amounts to about 43 mg. per liter. Below the surface it decreases rapidly so that at 50 meters depth (150 ft.) only 34 mg. are present per liter. At the bottom of the great deeps of the sea it again has increased to nearly 47 mg. per liter. One result of this increase in carbon dioxide concentration with great depth is that the flakes and shells of lime which are continually being produced by the organic life in the upper layers are generally dissolved on sinking into the lower layers of high carbonate concentration. At a depth of over 3000 meters (9000 ft.) no pteropod shells are to be found, while the more strongly built shells of globigerina are still present 5000 meters below the surface. On the ocean bottom less and less lime is to be found the greater the depth. At 900 meters the calcium content of the bottom mud is not less than 86%, at 4000 meters it is only 47%, at 6000 meters it is scarcely one percent, and in yet deeper regions there lies a red mud, colored by iron oxide," p. 145.

"In more recent years an experimental station with five mirrors of giant dimensions (60 by 4 meters) has been worked near Cairo, Egypt, with practical results. The builder was an American engineer named Shuman. The steam-pan was horizontal, as was the mirror axis. It was automatically turned so that the mirrors received the greatest possible radiation at all times of day. This plant was studied in 1913 by an authority, Ackermann. He found that its effectiveness was 60 h. p. per acre of earth-surface, over which the mirrors were mounted. The mirrors, in order not to hide one another in the morning and afternoon, must have space three times greater than their own actual open surface. Ackermann believed that the efficiency of these engines could easily be raised to 50%. In this event, and with the cost of construction and operation counted in, a horse power hour would cost about twenty cents and if the energy was changed to electric power this, in Cairo, should cost about 3.5 cents per kilowatt hour. This is a very moderate price. In Stockholm just before the war the price of lighting current was eight cents and power current four cents," p. 170.

"Great tracts of land in the Mediterranean countries, particularly areas near Avignon in France, which for many years previously had made great profit out of the growing of madder root, were forced by the competition of the synthetic product [alizarine] to give up this crop and had to be converted to the growing of other crops, naturally with great economic loss. However, seen from a more general point of view than that of the Avignon madder growers this must be looked upon as a benefit, for a fruitful district was thus returned to the ranks of bread-producing regions.

"Yet greater economic interests were ruined by the successful artificial production of indigo. This most important of all the dyestuffs has been in use from the grey dawn of antiquity by the Egyptians, the Phoenicians, and the Greeks. Indigo can be prepared from many different plants of which the most important is *Indigofera tinctoria*, a plant which originated in the East Indies but today is spread by cultivation into many parts of the tropics, in Asia, Africa and South America. Another indigo plant, *Isates tinctoria*, the *woad*, is much hardier and is to be found growing in Europe as far north as Sweden. It was formerly, especially around the year 1300, an object of intensive cultivation in France and

Germany, but as indigo began to be imported from the East Indies its European cultivation died out. Probably ancient man in Europe used the woad for a blue dye from very early times. The Pictish people of North Britain, when found by the Romans, were in the habit of painting their bodies for battle with woad. Indigo production in India in the past century was one of the most important sources of revenue of that country (and in consequence, of England). In 1897 the total value of natural indigo production was 20,000,000 dollars, and the amount was 6 million kilos of pure indigo, of which 90% came from British India," p. 219.

"The results [of the experiments on synthetic indigo] were most satisfying to the persevering workers. The importation of indigo into Germany sank from a value of fifty million dollars in 1896 to a value of eighty thousand dollars in 1911, while the export from that country for the same period mounted from thirteen to one hundred million dollars in spite of a drop in price to less than one-fifth. At the same time the value of the export of indigo from British India sank from seventeen to one million dollars. At one time the surface given over to the growing of indigo plant in India was not less than 1,480,000 acres," p. 220.

There are a few slips. Arrhenius still believes in the formation of a definite compound with caustic soda, p. 242, when cotton is mercerized. The translator says, p. 62, that bronze is made by adding a little copper to tin instead of the other way round. The proof reading is not very good and the translator shows a true Gallic freedom as to the spelling of proper names. Also, in English we do not speak of the beautiful blue Donau. The book is a very interesting one and Arrhenius preaches enthusiastically the doctrines of conservation.

Wilder D. Bancroft

Farbkunde. *By Wilhelm Ostwald. 22 × 15 cm; pp. xvi+313. Leipzig: S. Hirzel, 1923.* The book is divided into two parts: the general theory of color; and applications of the theory of color. In the first part the chapters are entitled: history of the theory of color; light; the process of seeing; the dull colors; the color circles; the symmetrical color triangle; the color fields; the doctrine of the color sector. Under applications we find three subdivisions: measurement of colors, with chapters entitled measurement of the dull colors, measurement of the color tint, measurement of the white and black content of the bright colors, and indirect measurements; physical-chemical relations, with chapters entitled the mixture of colors, physical chemistry of pigments and dyes, and the media for colors; psychophysical relations, with chapters entitled the physiology of the eye, color as a means of representation, and the harmony of colors.

Ostwald recognizes eight main colors: yellow, orange, red, violet, ultramarine blue, ice blue, sea green, and leaf green. He omits the orthodox indigo which only very few people see and splits blue and green into two colors each. Each one of these main colors he divides into three, red into vermilion, carmine, and the purple of the dark red roses; and ultramarine blue into the blues of ammoniacal copper solution, of ultramarine, and of the blue of the sky, p. 91. Starting with 3-5% solutions of quinoline yellow, eosine, rose Bengale, wool blue, and Neptune blue, one can duplicate almost any pure color by dipping pieces of white filter paper either into these solutions or into suitable mixtures of them, p. 76.

Ostwald constructs triangular diagrams with white, black, and any pure color in the three corners, p. 94. He calls attention to the great beauty of the clear colors with a good deal of black in them and claims that the beauty of the old church glass is due either to dust which blackens them or to the presence of magnetite in them to darken them. While this is undoubtedly true to a great extent, striae and irregularities in thickness add also to the beauty of the old glass as was shown conclusively by LaFarge.

Ostwald lays great stress on the theoretical significance of what he calls the "Farbenhalb" or color sector, p. 117. The best yellow is not one which transmits only the spectrum yellow; but one which transmits all the light from red to sea-green so that one gets the synthetic yellow from red and green superposed on the spectrum yellow. In other words the important color sector is the one which includes the colors on either side which make the color under discussion when combined.

The color sectors of the warm colors, leaf-green, yellow, orange (which Ostwald calls Kress) and red contain a good deal of white, which one does not notice as such, while the color sectors of the cool colors, violet to sea-green contain a good deal of black. In fact it is the presence of white in the saturated colors of one class and of black in the saturated colors of the other class which gives rise to the terms warm and cool.

Ostwald points out, p. 126, that when one mixes two complementary colors by means of a rotating disc, the resulting white is spread over twice the surface and is therefore actually gray. If colored lights are mixed, one can get either white or gray, according to the background. On p. 186 Ostwald shows that the colors from orange to blue all move towards the green on dilution while red moves towards the violet. Ostwald believes strongly in five-color printing as against three-color printing, p. 192, if one wishes to reproduce colors satisfactorily.

On p. 202 Ostwald states that white lead is a mixture of lead carbonate and lead hydroxide, and that the two can be distinguished under the microscope. This is of course a mistake. White lead is basic lead carbonate. The commercial pigment may contain an excess of lead carbonate or of lead hydroxide; but that is not what Ostwald said. The reviewer also finds it impossible to accept Ostwald's remarks on luster, p. 36. "Most actual surfaces lie between the two extremes of complete specular reflection and completely matte surfaces. If the specular reflection is recognizable, one calls the surface lustrous, the luster increasing with the amount of specular reflection. Fatty luster, vitreous luster, adamantine luster, and metallic luster are arranged in the order of increasing specular reflection."

Warm glazing colors remain transparent even in thick layers while the black in cold glazing colors makes them look black in thick layers, p. 207. Ostwald proposes to take as the standard of reduction with white the amount of zinc oxide which must be added to one gram of a pigment to give an optical white content of fifty percent. This will be 0-30 with the mineral pigments and may run over 1000 with the dyes, p. 212.

When a pigment is ground, there is a grain size for which the color is most intense, because too much white is reflected when the pigment surface is increased too much. It follows from this that the pigments which can stand the most reduction with white can stand the finest grinding. For cobalt glass the most effective grain size is 0.5-1.0 mm.

Ostwald is an authority on the theory of colors; but he slips up when he talks about dyeing, p. 247. Basic and acid dyes are not colloidal and they don't dye cotton direct. Substantive dyes do dye cotton direct and are in colloidal solution. No one would guess from what Ostwald says that sodium sulphate acts in three ways with the three classes of dyes: basic, acid, and substantive. There is another unfortunate statement on p. xvi. "The blue color of the sky is due to physical and not to special chemical causes. All earthly objects on the other hand show chemical colors." Ostwald has forgotten or never known about the blue feathers of birds, the moonstones, the iridescent feathers, the temper colors on steel, etc.

Ostwald lays down the general rule, p. 271, that in all fields of art law is harmony. "In a book entitled "The Harmony of Forms," which appeared in 1922, I tried out the experiment thoroughly. The classification was found to cover all the previous laws of ornamentation and of beautiful forms as they have been worked out by artists during thousands of years and it also enabled the prediction of an infinite number of beautiful forms which the creative phantasy of all the people in all times had not originated, and there was not a single ugly one among them," p. 273.

It is often said by dressmakers and decorators that white and black harm no colors. Otswald takes issue with this, p. 282. He claims that white goes well only with the bright clear colors. One can combine white with pink or sky blue, with vermilion or ultramarine blue; but one cannot combine white with bottle green, a blackish blue, or a yellow containing black. One corollary is perhaps subject to the decrees of fashion. "Another case is that children and very young girls can wear white while it is not suitable as the chief color for older women. The reason for this is that from about twenty-five years on the skin becomes darker due to increase of coloring matter in the surface cells, and this increasing amount of black makes the complexion appear muddy when contrasted with white, whereas colors containing more black make the skin appear clearer."

Conversely, black goes well only with colors which are poor in white. Since red is the one of the bright colors which can most easily be obtained in a deep shade with a low white content this accounts for the fondness people have for combining black and red.

Wilder D. Bancroft

A System of Physical Chemistry. *Vol. II. Thermodynamics. Fourth edition. By W. C. McC. Lewis. 22 × 15 cm; pp. viii+489. New York and London: Longmans, Green and Co., 1925. Price: $4.75; 15 shillings.* Whilst all chemists who are not faddists agree that a knowledge of Thermodynamics is useful and even necessary in a proper understanding of the modern science, they will also admit that perhaps no other branch of the subject offers such difficulties to the average student. It may not be impossible that these difficulties are introduced by a particular treatment of the subject. By avoiding terse and clear-cut statements, adopting a discursive style, interpolating explanatory paragraphs to break up an argument, and returning to a subject again and again after having given the impression that it has been brought to a conclusion, modern thermodynamics might conceivably be robbed of its main terror, that of being a science capable of leading, by strictly logical development from two general laws of experience to a great number of special results without the aid of loose analogical or ingenious but shaky hypotheses. There is little doubt that a logical way of treating the subject is distasteful to the average student of chemistry and the author of a successful textbook will, in the interests of popularity, be careful to avoid it.

Professor Lewis's book is too well known to need description. In its fourth edition he has made certain slight alterations and has added new sections which much enhance its value. A readable account of recent American work is given, but European contributions are not altogether neglected. In some cases the treatment has been made rather stricter, notably in the direction of the equation of maximum work. Whilst this is perhaps desirable on scientific grounds it will reduce to some extent the popularity of the book, since the new treatment is rather more difficult to follow than the old, although more accurate. No attempt is made to preserve a consistent set of symbols throughout, but although this might puzzle a mathematical student it will perhaps enhance the clearness of the work to a student of chemistry. This result is also inevitable if the author's practice of quoting original papers almost *verbatim* is followed. The symbols are always clearly defined.

Sections which may be especially commended are those on electromotive force, on activities (in which the recent memoir of A. A. Noyes on the Debye-Hückel theory is reproduced *verbatim*), theory of membrane equilibria, and chemical affinity. A special feature is the inclusion of modern work, and numerical results are freely quoted. This makes the book very useful for reference purposes. Whilst it has not the wealth of numerical data of Lewis and Randall, nor the strict but arid mathematical elegance of Gibbs, it succeeds in giving the impression, by a skilful interweaving of theory with the results of experiment, that thermodynamics is a living science of great value to chemists. This is a really praiseworthy achievement, for which the author deserves, and will receive, the congratulations of his fellow-chemists.

J. R. Partington

THE CHEMICAL ACTION OF α PARTICLES ON ACETYLENE

BY W. MUND AND W. KOCH

Having found in previous work[1] that acetylene gas when mixed with radon is slowly converted into a pale yellow powder, we investigated further[2] by a simple method the rate of such polymerization. The quantitative results were worked out:

1. Knowing the number of α particles emitted by a given quantity of radon with equilibrium amounts of RaA and RaC (1 curie gives $3 \times 1.772 \times 10^{16} (1 - e^{-\lambda t})$ particles.

2. Taking into account the partial absorption of the α particles by the walls, RaA and RaC being wholly deposited.

The formula we used[3] rested upon the validity of Geiger's ionization law. We calculated thus that, at 0°C and at a pressure of about 70 cm. of mercury, every α particle emitted by radon (range 3.94 cms.) brings about the condensation of 4.38×10^6 gaseous molecules. The total ionization along the path of an α particle in acetylene being 2.13×10^5, it follows that for each ion, 20.5 molecules fall out.

As S. C. Lind[4] first suggested, the ratio M/N is often near unity, M being the number of reacting molecules and N the number of ions produced. This led M. Bodenstein[5] to correlate the radiochemical reactions which follow the rule with his primary photochemical reactions. In the case of acetylene, however, the M/N ratio is much larger than in most other primary reactions, though much smaller, indeed, than in the HCl synthesis, which Bodenstein compares with a photochemical secondary reaction. Thus arose the question to which class the acetylene polymerization would belong from other points of view, namely, as regards the influence of oxygen, pressure and temperature.

I. The Influence of Oxygen

A system of two identical bulbs, B_1 and B_2, surrounded by melting ice was connected by a U shaped tube, which acted as a differential manometer, Fig. 1. Acetylene was admitted, its pressure being at first equal on both sides. While mercury in connection with B_1 was kept at constant height, its level slowly rose in the other branch of the manometer as soon as a known quantity of radon had been introduced into B_2 (by a device not shown on Fig. 1). The difference of height being h and the difference of volume V−V′, the pressure in B_2 reduced to constant volume is expressed by

$$P' = (P - h)\ V'/V$$

---

[1] Mund and Koch: Bull. Soc. chim. Belg. **34**, 119 (1925).

[2] Bull. Soc. chim. Belg. **34**, 241 (1925).

[3] Mund: Ann. Soc. scient. Bruxelles, **64**, 336 (1925).

[4] Lind: J. Phys. Chem. **16**, 564 (1912).

[5] Bodenstein: Z. physik. Chem. **85**, 390 (1913).

The experiment was started without any oxygen in B_2. At time t_1 and t_2, the pressures P'_1 and P'_2 were noted showing (c.f.i.) that 4.07×10^6 molecules condensed per α- particle (of range 3.94 cm). The agreement with former experiments is close enough to exclude accidental disturbance.

The same experimental contrivance (not shown in Fig. 1) that had provided for the introduction of radon, was now used to bring into B_2 about 8 cm³ of air (i.e., 2 cm³ of o_2). As will be seen from the table below, the decrease of pressure is at first slightly accelerated. After a few hours, however, it proceeds at its primitive rate. Counting time from the introduction of the air, we found between t_1 = 8h.10′ and t_2 = 21h.30′, a rate of condensation of 4.22×10^6. Between t_1 = 10h.40′ and t_2 = 31h.15′ after a second introduction of air we found 4.17×10^6.

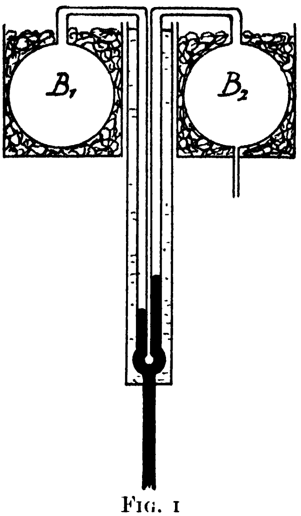


FIG. 1

The small increase of reaction velocity just after the addition of air might easily be explained. The air entering B_2 at a temperature of about 20°C, cools down and contracts. Further on, part or totality of its oxygen will perhaps be adsorbed as one knows that cuprene does retain large amounts of it.

Let M be the number of C_2H_2 molecules condensing and L the number of α-particles which—running undisturbed through the whole range (of 3.94 cm. in air)—would supply such ionization or chemical effect as really happened in B_2. The number M of molecules brought into reaction by each of these α-particles will be

$$m = M/L$$

M is a product of three factors: (1) the proportional decrease of pressure; (2) the number of gram-molecules in B_2; (3) the Avogadro number (as given by R. Millikan). Thus:

$$M = \frac{P'_1 - P'_2}{P'_1} \times \frac{V\,P'_1\,273}{22412(273+t)76}, \times 6.06 \times 10^{23}$$

Putting V = 550 cm³ and t = 0

$$M = (P'_1 - P'_2) \times 1.957 \times 10^{20}$$

L is given by

$$L = N_0\,(1 - e^{-\lambda t})F$$

N_0 is the number of radon atoms present at the outset (t — 0) and is equal to 1.772×10^{16} times the initial number of curies. F is calculated from the following formula which takes account of the α-particles from RaA and RaC as well as of the absorption undergone by α-particles hitting the wall. Let r, r′, r″ be the ranges of α-particles from radon, RaA, RaC, respectively. As long as the diameter 2 R of the bulb B_2 exceeds r″, we have:

$$F = \left\{1 + \tfrac{1}{2}\left(\frac{r'}{r}\right)^{2/3} + \tfrac{1}{2}\left(\frac{r''}{1}\right)^{2/3} - \frac{9r + 3\left(\frac{r'}{r}\right)^{2/3}r' + 3\left(\frac{r''}{r}\right)^{2/3}r''}{20\,R} + \frac{81}{3520}\left(\frac{r}{R}\right)^{3}\right\}$$

In air at 0°C and normal pressure $r = 3.94$; $r' = 4.50$; $r'' = 6.57$. The stopping power of acetylene amounts to 112/100.

$$F = 2.249 - 0.989\, r/R + 0.023\, (r/R)^3.$$

The range r should be calculated from the mean pressure

$$P_m = 0.5\, (P'_1 + P'_2) \text{ by the relation}$$

$$r = \frac{3.94}{1.12} \times \frac{76}{P_m} \times \frac{273}{273 + t} \quad (t = 0)$$

This involves no other assumption than inverse ratio between the range and the number of molecules encountered per cm by the α-particle.

$N_0 = 1.0146 \times 10^{15}$ (0.05726 curie); $P = 67.65$.

Time: t	Corrected pressure: P′	m
t_1 = 47.50 hours	64.23 cm.	4.07×10^6
t_2 = 43.75	63.86	
(first introduction of air)		
t_3 = 44.00 hours	65.06 cm.	
t_4 = 44.42 hours	64.98 cm.	
t_5 = 44.75 "	64.00 "	
t_6 = 45.33 "	64.77 "	
t_7 = 46.08 "	64.64 "	
t_8 = 46.90 "	64.55 "	
t_9 = 47.75 "	64.42 "	
t_{10} = 49.25 "	64.17 "	
t_{11} = 51.92 "	63.74 "	4.22×10^6
t_{12} = 65.25 "	61.74 "	
(second introduction of air)		
t_{13} = 65.70 hours	62.86 cm.	
t_{14} = 66.17 "	62.75 "	
t_{15} = 66.90 "	62.66 "	
t_{16} = 67.80 "	62.55 "	
t_{17} = 70.25 "	62.24 "	
t_{18} = 73.47 "	61.77 "	
t_{19} = 75.93 "	61.46 "	4.17×10^6
t_{20} = 96.50 "	59.03 "	

II. Influence of Pressure

As the decrease of pressure owing to the progress of the reaction amounts easily to 40% (with the size of bulb B_2 and the radon at our disposal), it will suffice to run the experiment a fairly long time (without adding air) in order to ascertain the effect of changing pressure. The following data refer to an experiment which lasted 17 days. Though fluctuating, the values of m do not vary in a systematic manner. It may thus be said that the rate of reaction is not appreciably affected by change of pressure. (At very low pressures recoil atoms would of course play their rôle.)

$$N_0 = 1.022 \times 10^{15}\ (0.0661\ \text{curies});\ P = 67.75\ \text{cm.}$$

Time t		Corrected Pressure P′	m
$t = 0$	hours	67.75 cm.	4.24×10^6
$t_1 = 24.66$	”	62.33	4.17×10^6
$t_2 = 48.16$	”	58.27	4.33×10^6
$t_3 = 72.00$	”	54.83	4.30×10^6
$t_4 = 121.16$	”	49.73	4.27×10^6
$t_5 = 167.66$	”	46.62	4.45×10^6
$t_6 = 239.50$	”	43.52	4.23×10^6
$t_7 = 312.00$	”	41.88	4.67×10^6
$t_8 = 409.08$	”	40.63	

III. Influence of Temperature

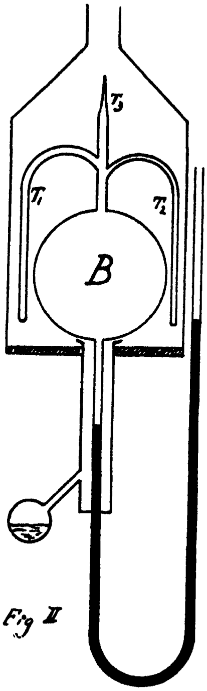


FIG. 2

Our apparatus[1] (Fig. 2) was an open air manometer connected with a glass sphere B (R = 3.40 cm.) In the upper part of this sphere ended:

1. Two small pieces of glass tubing, bent downwards, and closed at the other end; one of them, T_1, immersed in liquid air, held an adequate quantity of C_2H_2 in the condensed state. The other, T_2, contained a known amount of well-purified radon enclosed under a capillary column of mercury.

2. A drawn-out tube, T_3, connecting B with a Langmuir vacuum pump.

The bulb, B, having been evacuated, the tube T_3 was sealed off, and the tube T_2 was heated till all the mercury boiled over to B causing the radon to diffuse. Then the liquid air was withdrawn allowing the acetylene in T_1 to evaporate and to fill B at nearly atmospheric pressure.

The bulb B, along with the tubes, T_1, T_2 and T_3 and the copper part of the manometer tube, was then kept at 100°C by means of a steam bath securing a very good constancy of temperature. Pressure measurements at 100°C having been completed, the steam was removed and another set of readings was taken at 20°C and at 0°C.

The volume of the sphere B was only 164 cm³, but taking into account the capacity of T_1, T_2, T_3 and of part of the manometer stem, the total volume V of the gaseous mixture amounted nearly to 190 cm³. The initial and final pressure, P_1 and P_2, of every measurement were given by the manometer, the atmospheric pressure being read at the same time on a good mercury barometer.

---

[1] For full details see Mund and Bogaert: Bull. Soc. chim. Belg. **39**, June (1925).

The number m was calculated as before by the relation $m = M : N_o(1 - e^{-\lambda t}) F$.

In the experiment at 100°, the factor F could be calculated by the formula applying when $2R > r''$, but at 20°C and at 0°C the pressure was so far reduced as to require another formula fitting the conditions $r'' > 2R > r'$, namely:

$$F = 1 + \tfrac{1}{2}\left(\frac{r'}{r}\right)^{2/3} + 1/2\left(\frac{r''}{r}\right)^{2/3} - \frac{9r + 3\left(\frac{r'}{r}\right)^{2/3} r' + 3\left(\frac{r''}{r}\right)^{2/3} r'' - 3\left(\frac{r''-2R}{r}\right)^{2/3}(r'' - 2R)}{20\,R} + 81/3520\,(r/R)^3$$

In every case, however, the factor F had to be corrected owing to the fact that 26 cm³ (i.e., 13.6% of the total volume of 190 cm³) did not belong to the sphere B but were contained in narrow shaped glass tubes. This resulted in a loss of ionization which could be estimated and for which allowance was made by reducing the factor F to 9/10 of its value. It will be gathered from the results that change of temperature as well as of pressure has but little, if any, influence on the reaction velocity.

$N_o = 8.1725 \times 10^{11}$ (0.04612 curie)

Time	Pressure	Temperature	m
t_1 = 12.16 hr.	87.18 cm.	100°C	4.17×10^6
t_2 = 20.16 "	73.68	"	"
t_3 = 20.75 "	65.63	20°C	4.28×10^6
t_4 = 44.33 "	59.08	"	"
t_5 = 60.75 "	49.04	0°C	4.41×10^6
t_6 = 67.92 "	48.86	"	"

Conclusions

I. No variation exceeding experimental error could be detected in number of molecules of acetylene polymerized per pair of ions produced in the system (1) at different pressures; (2) at different temperatures; 0°C, 20°C, and 100°C; and (3) in the presence of small quantities of air.

II. Taking the general mean value of eleven measurements (without oxygen) obtained in this study and two concordant measurements previously reported, the ratio of the number of molecules of acetylene polymerized per pair of ions produced ($-MC_2H_2/N$ total) is 20.2.

Louvain
Laboratory of Physical Chemistry
of the University,
September, 1925.

THE INFLUENCE OF IONS CARRYING THE SAME CHARGE AS THE DISPERSED PARTICLES IN THE INVERSION OF EMULSIONS

BY S. GHOSH AND N. R. DHAR

In previous papers[1] we have emphasised that the stability of a sol depends a great deal on the adsorption of ions carrying the same charge as the sol. We have also suggested that ions carrying the same charge as an emulsion influence the stability of the emulsion markedly. In this paper we shall show that ions carrying the same charge as the emulsoid particles have a considerable influence on the inversion of the type of an emulsion.

The investigations of Lewis,[2] Ellis,[3] Powis[4] and others show that the emulsoid particles are charged and that their stability depends upon the electric potential at the surface of the globules, just as colloids remain suspended due to their electric charge.

Powis studied the effect of KCl, K_4 Fe(CN)6, $BaCl_2$ $AlCl_3$ and $ThCl_4$ on the velocity of oil particles dispersed in water under an electric field. For the pure emulsion, the velocity, of the particles first increased when KCl or $K_4Fe(CN)_6$ was gradually added and with greater amounts of these electrolytes it fell. A similar maximum was observed by Ellis in the presence of 0.001N NaOH. On the other hand, the velocity of the oil globules gradually fell when $BaCl_2$, $AlCl_3$, or $ThCl_4$ were added and finally they moved in the opposite direction showing a reversal in charge. Similar results were obtained by Powis using As_2S_3 sol and KCl, Kruyt[5] with As_2S_3 sol and KCl, and Freundlich and Zeh[6] with As_2S_3 sol and K_4 $Fe(CN)_3$, and with $Fe(OH)_3$ sol and $\left[\left(NH_3\right)_4 Co \left\langle {NH_2 \atop OH} \right\rangle Co \left(NH_3\right)_4\right] Cl_4$ where first an increase in velocity was observed on the addition of the electrolytes.

We have already indicated that this increase in velocity is a direct consequence of the adsorption of an ion carrying the same charge as the suspended particles on the addition of these electrolytes, in spite of the fact that there exists an electric repulsion due to the sameness of the electric charge. Let us consider the fate of an electrolyte say KCl, when added to a negatively charged colloid. Now, if the tendency for adsorption of similarly charged Cl' ions is greater than the force of repulsion due to the sameness of electric charge, the charge on the colloid particles will increase as chloride ions are adsorbed, when small quantities of KCl are added. This increase in velocity, however, reaches a limit when the adsorption of chloride ions is maximum and the adsorption of the oppositely charged K ion increases. If, however, the adsorption of chloride ions cannot counter-balance the repulsive effect due to the sameness in electric charge we may not get any marked increase in the velocity of the colloid particles in an electric field, but the fall in the velocity of the colloid particles when KCl is added to the sol will not be rapid. On the other hand, if the adsorption of similarly charged chloride ions is comparatively small or nil, the fall in the velocity of the colloid particles will be rapid on the continued addition of small quantities of KCl.

---

[1] Ghosh and Dhar: J. Phys. Chem., **29**, 435 (1925); Ghosh, Bhattacharya and Dhar; Kolloid-Z. (1925).

[2] Phil. Mag. (6) **15**, 509 (1908).

[3] Trans. Faraday Soc. **2**, 14 (1913).

[4] Z. physik. Chem. **89**, 91 (1914).

[5] Kolloid-Z. **22**, 81 (1918).

[6] Z. physik Chem. **114**, 65 (1924).

Consequently, from the results of Powis we can infer that oil particles in water are negatively charged and appreciably adsorb ions carrying the negative charge from such electrolytes as KCl, $K_4Fe(CN)_6$, etc.

It has already been indicated that emulsions closely resemble colloidal suspensions. From the existing literature we find that emulsions behave abnormally towards electrolytes on dilution that is become more stable towards electrolytes on dilution. This behavior is certainly due to the adsorption of ions carrying the same charge as the oil globules. It is expected therefore that such emulsions would also show (i) abnormality towards a mixture of electrolytes i.e. show an antagonistic effect when coagulated by a mixture of electrolytes of varying valency, and (ii) the phenomenon of acclimatization.

Bhatnagar's[1] results on the coagulation of aniline emulsion show that it becomes stable on dilution towards electrolytes such as KCl, $BaCl_2$ and $Al_2(SO_4)_3$. His results are given in Table I.

TABLE I

Electrolyte added		Time of Perceptible Change in Emulsion							
Grms equivs. per litre		Emulsion		Twice diluted		Three times diluted		Four times diluted	
		Mins	Secs.	Mins.	Secs.	Mins	Secs.	Mins.	Secs.
KCl	(a) 0.1	41	0	56	1	115	5	133	10
	(b) 0.139	12	8	20	5	41	0	63	9
$BaCl_2$	(a) 0.029	10	0	18	7	27	5	40	0
	(b) 0.040	2	0	4	6	7	0	13	2
$Al_2(SO_4)_4$	(a) 0.002	10	0	11	1	13	5	15	9
	(b) 0.005	2	0	2	53	3	58	7	2

We have shown that with all the suspensoids so far studied in this laboratory the tervalent $Al^{\cdots}$ ion always behaves normally towards dilution. This behavior of $Al^{\cdots}$ ion with aniline emulsion will be discussed later on.

In the following pages more evidence will be advanced in favour of the view that an emulsion can adsorb an ion or a micelle carrying the same charge as the emulsiod particles and it will be shown that our generalisation already referred to is more or less followed by emulsions.

Very little systematic work has been done on the coagulation of emulsions by electrolytes. Hence it is difficult to draw very definite conclusions regarding the effect of anions on the precipitation of an emulsion.

---

[1] J. Phys. Chem. 25, 735 (1921).

It is obvious that when an emulsion is formed of two immiscible liquids say water and oil, it is possible to get two kinds of emulsion viz, (i) oil dispersed in water and (ii) water dispersed in oil. The existence of such two types of emulsions has been recognised by Ostwald,[1] Robertson[2] and other. Bancroft[3] has shown that sodium oleate emulsifies oil in water and calcium oleate emulsifies water in oil. The systematic work of Newman,[4] Briggs and Schmidt,[5] Clowes[6] and others on the inversion of oil-in-water emulsion to water-in-oil type has thrown considerable light on this question.

Clowes has shown that an oil-in-water emulsion produced in the presence of sodium soap can be inverted into water-in-oil emulsion by the addition of a calcium salt. The transformation of an oil-in-water emulsion to a water-in-oil emulsion by means of a calcium salt has been followed microscopically. It is noted that the oil globules in water are first distorted, then elongated and as the critical point for inversion of phases approaches the Brownian movement is very marked, and finally on complete conversion of the system into an emulsion of water in oil, the Brownian movement of these oil particles dispersed in water entirely ceases. From these observtions it can be concluded that at the critical point of the inversion of the type the coagulation of oil-in-water emulsion has set in and that the emulsion is extremely unstable.

It seems that up till now very little attention has been paid to the question of charge on emulsoid particles. Several workers have shown, however, that the usual charge on the suspended oil particles is negative. We are of the opinion that when the electrolytes like KCl, NaCl, etc., are added to such an emulsion, at first preferential adsorption of the negative ions takes place and consequently the negative charge on the oil globules increases. If the concentration of such electrolytes is increased the influence of the oppositely charged ion becomes more prominent and the charge on the oil globules is neutralised and is followed by the coalesence of the oil globules to form bigger drops and separation into two layers. This phenomenon is the same as the coagulation of a sol by the addition of an electrolyte.

It is interesting to note that reversion of emulsion oil-in-water to water-in-oil hardly takes place with KCl, NaCl, etc., but phase-reversal of oil emulsions takes place readily with bivalent and trivalent cations and H ions. Consequently, we are of the opinion that in water-in-oil emulsion the dispersed water particles are positively charged. This is further supported by the observation of Bancroft that in the presence of sodium or potassium oleate oil-in-water emulsion is obtained, whilst in the presence of calcium or magnesium oleate water-in-oil emulsion is formed. Moreover Bhatnagar[7] has obtained phase-reversal of water-in-oil by KOH, K_3PO_4, etc.

[1] Kolloid-Z. **6**, 103 (1910); **7**, 64 (1910).

[2] Kolloid-Z. **7**, 7 (1910).

[3] "Applied Celloid Chemistry," 267 (1921).

[4] Phys. Chem. **18**, 34 (1914).

[5] J. Phys. Chem. **19**, 478 (1915).

[6] Proc. Soc. Exp. Biol. Med. **11**, 1 (1913); J. Phys. Chem. **20**, 407 (1916).

[7] J. Chem. Soc. **129**, 1760 (1921).

This is due to the fact that the oil particles have a tendency to adsorb oleate ions and pass into negatively charged oil-in-water emulsion, whilst water particles have a tendency to adsorb $Mg^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ ions and pass into positively charged water-in-oil emulsion. There are certain points of resemblance between the phase-reversion of emulsion and charge-reversal of colloids. It is well known that the charge reversal of a sol usually takes place by a bivalent or a polyvalent ion or $H^{\cdot}$ or OH' ions; similarly, reversion in phase of emulsion also occurs with bivalent and polybalent ion or $H^{\cdot}$ and OH' ions. Let us see what happens when $CaCl_2$ is added to an emulsion of oil-in-water. The $Ca^{\cdot\cdot}$ ion will be adsorbed by the particles of the oil on charge-neutralisation and coalesence of the oil globules will take place. Just before the separation of the substances in two layers, the water particles, which have a greater affinity for $Ca^{\cdot\cdot}$ ions than that of oil particles for the same ion, will take up $Ca^{\cdot\cdot}$ ion and pass into positively charged water particles forming a water-in-oil emulsion, provded the system is shaken well. This is possibly the mechanism of phase-reversal of an emulsion by a polyvalent ion. It is evident that in the case of charge reversal of a sol only the charge on the suspended particles is changed, whilst in the case of phase reversal the dispersed phase is different in the two conditions.

Clowes showed that in the case of emulsions of olive oil in water stabilised by NaOH, the addition of $CaCl_2$ leads to the inversion of the type. Table II gives the results obtained by Clowes with olive oil emulsion containing free oleic acid.

TABLE II

Vol. of M/10 NaOH added. c.c.	Vol. of M/10 $CaCl^2$ employed. c.c. 0.25	0.5	0.75	1.0
1	R	W-O	W-O	W-O
2	O-W	R	W-O	W-O
3	O-W	O-W	R	W-O
4	O-W	O-W	O-W	R

O-W = Oil-in-water emulsion.
W-O = Water-in-oil emulsion.
R = Critical (inversion) point.

These results show that the greater the concentration of the added NaOH the, greater is the amount of $CaCl_2$ required to bring about the inversion of the emulsion. On plotting the logarithims of NaOH added as abscissae and the logarithims of the corresponding amounts of $CaCl_2$ to bring about the inversion of the emulsion as ordinates, we find that the graph is a straight line, showing that the adsorption formula of Freundlich,[1] $x/m = KC^n$, where x = the amount adsorbed by m grams of the adsorbent, C = concentration of the solution and k and n are constants, is strictly followed. This therefore, simply proves that the stabilisation of the oil-in-water emulsion is due to the adsorption of OH' ions from NaOH or oleate ions from sodium oleate formed by the action of NaOH and free oleic acid.

---

[1] Kolloid-Z. **3**, 212 (1908).

Clowes has also shown that the adsorption of ions is the underlying factor in emulsion equilibrium. Besides $CaCl_2$ Clowes has observed that bivalent salts of Mg,$^{\cdot\cdot}$ Sr$^{\cdot\cdot}$ and Ba$^{\cdot\cdot}$ and trivalent salts of Al$^{\cdot\cdot\cdot}$ and Fe$^{\cdot\cdot\cdot}$ exert an effect similar to that of Ca$^{\cdot\cdot}$, whilst KOH, LiOH, etc., may be substituted for NaOH.

The effect exerted on emulsions by KCl, NaCl, sodium citrate, etc., is very interesting. It has been observed by Clowes that NaCl in small quantities promotes the formation of emulsions of oil-in-water and improves the dispersion of the oil, so that more $CaCl_2$ is necessary to bring about the inversion of the emulsion in the presence of small amounts of NaCl. Apparently this has to be ascribed to the preferential adsorption of negatively charged Cl$'$ ions from NaCl by the negatively charged emulsoid particles or by the soap film adhering to the oil particles. He has also shown that when NaCl is added to an emulsion up to a concentration of 0.1M preferential adsorption of chloride ions takes place and thus facilitates the formation of oil emulsion and dispersion of oil globules. At higher concentrations of NaCl the adsorption of negative ions in excess to that of positive ions does not occur to the same extent, and at 0.35 M to 0.40 M NaCl the emulsion separates in two layers; that is, coagulation sets in.

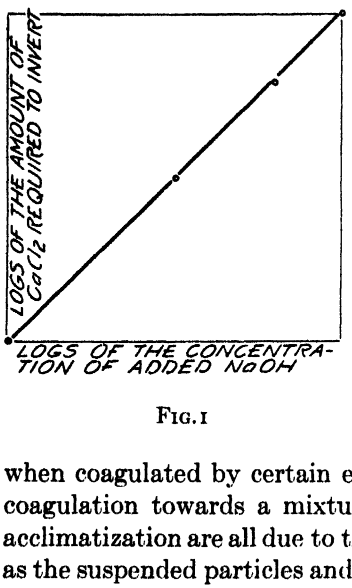


Fig. 1

These observations of Clowes are in support of our postulation that (i) stability of the sols and emulsions towards dilution when coagulated by certain electrolytes (ii) antagonistic effect observed on coagulation towards a mixture of electrolytes and (iii) the phenomenon of acclimatization are all due to the adsorption of an ion carrying the same charge as the suspended particles and are essentially connected and go hand in hand. It is well known that when As_2S_3 sol[1] is coagulated by a mixture of KCl and $BaCl_2$, LiCl, and $BaCl_2$, etc., the previous addition of KCl or LiCl makes the sol stable, and more of $BaCl_2$ is necessary to bring about coagulation than when $BaCl_2$ coagulates the sol alone. In a previous paper we have observed that this is due to the adsorption of chloride ions by As_2S_3 sol from KCl, when added in small quantities, in spite of the fact that there exists an electric repulsion due to the sameness in the electric charge. As the amount of KCl added is gradually increased the adsorption of chloride ions reaches a maximum. On the further addition of KCl, the adsorption of K ions greatly exceeds that of the chloride ions and the sol is finally coagulated by KCl. It is, therefore, obvious that a point of maximum stability exists as KCl is gradually added to the sol. From the experiments of Linder and Picton, Weiser and others, it will be seen that the amount of $BaCl_2$ or $SrCl_2$ necessary for the complete coagulation goes on increasing with the increase in the concentration of KCl up to a limiting value. After this limiting value is attained if the concentration of KCl is further increased the amount of $BaCl_2$ or $SrCl_2$ necessary for complete coagulation gradually diminishes.

---

[1] Linder and Picton: J. Chem. Soc. **67**, 67 (1895); Weiser: J. Phys. Chem. **25**, 665 (1921); Ghosh, Bhattacharya and Dhar: loc. cit.

From these results a very interesting point has been drawn out in a previous paper.[1] It is well known that keeping the amount of the adsorbent constant, the greater the concentration of the electrolyte which will be adsorbed the greater is the amount of adsorption. Now, as the concentration of the electrolytes KCl, LiCl, etc. is increased the adsorption of Cl ions goes on increasing and thus the sol becomes more and more stable. We expected that up to this maximum stability the Freundlich exponential formula for adsorption should be followed, where the concentration of KCl added may be roughly taken as the final concentration of the electrolyte and the excess of $SrCl_2$ necessary for coagulation in the presence of KCl as the amount proportional to the adsorption of chloride ions. Beyond this maximum stability the adsorption of K ions becomes more prominent and, therefore, the adsorption formula need not be followed. We have shown that on plotting a graph with Linder and Picton's result by taking the logarithims of the excess of $SrCl_2$ necessary for complete coagulation as ordinates and the logarithims of the amount of KCl added as abscissae a straight line is obtained. This proves conclusively that chloride ions are preferentially adsorbed by As_2S_3 sol. The similar graph obtained for the inversion of oil-in-water emulsion by $CaCl_2$ in the presence of NaOH shows that this stabilisation of the emulsion in presence of NaOH is not materially different from that of As_2S_3 sol in the presence of KCl, though more markedly.

Clowes has classified electrolytes into two main groups (1) promoting dispersion of oil-in-water salts of monovalent cations Li, Na, K, etc., alkalies, salts of divalent and trivalent anions, (2) promoting dispersion of water-in-oil—salts divalent and trivalent cations Ca, Ba, Sr, Fe, Al, etc. It has been already indicated that the system water-in-oil may be looked upon as coagulated oil-in-water emulsion, and therefore can be compared to a jelly, where water is dispersed in the continuous solid phase.

Hardy[2] believed that the concentrated gelatine jellies consisted of drops of water suspended in a gelatine-rich phase. Many workers are, however, of the opinion from the ultramicroscopic observations that jellies have a sponge structure and not a honeycomb structure peculiar to emulsion jellies, where water is the dispersed phase; but it is now believed that we cannot distinguish between the two cases by means of the ultramicroscope.[3]

If we regard a water-in-oil emulsion as coagulated oil-in-water emulsion, salts like NaCl, KCl, $K_4Fe(CN)_6$ etc., promote the formation of the emulsion oil-in-water due to the adsorption of similarly charged ions like Cl', $Fe(CN)_6''''$ etc., whilst the salts of bivalent and trivalent cations can easily coagulate the oil particles and help the dispersion of water particles as a positively charged water-in-oil emulsion.

---

[1] Ghosh and Dhar: J. Phys. Chem. **29**, 435 (1925).

[2] Z. physik. Chem. **33**, 326 (1900).

[3] Compare Bachmann: Kolloid-Z. **23**, 89 (1918).

Clayton[1] has also observed that monovalent salts like KCl, NaCl, etc., help the emulsification of oil in water. He has observed that 1% NaCl greatly facilitates the formation of margarine emulsion in water. This is ascribed by Clayton to the adsorption of chloride ions from NaCl and subsequent liberation of NaOH, which forms soap with the free oleic acid already present. Similar effects of monovalent cations have been observed by Ayres[2] and Herschel[3] on the formation of oil-in-water emulsion. We are of the opinion that in all these cases the charge on the oil particles and the degree of dispersions are increased due to the adsorption of small quantities of Cl' ions. Briggs[4] on the other hand has observed that NaCl possesses no emulsion-producing property with benzene.

Recently Rosner and Narrat[5] have shown that a 25 cc mixture of rape oil and mineral oil forms a stable emulsion with 25 cc of sea water, where water forms the continuous phase. The emulsion is fairly stable showing that the emulsification is greatly helped by the NaCl of sea-water. Increase in the amount of sea water is unfavourable towards emulsification. Harkins and Keith[6] have also shown that the addition of potassium iodide or sodium chloride decreases the size of the dispersed oil particles; and this shows that an oil emulsion is stabilised by the addition of monovalent electrolytes due to the adsorption of the similarly charged anions.

The experiments of Parson and Wilson[7] are also of much interest from this point of view. Using emulsions of pure mineral oil 'Nujol' in the presence of a dilute sodium oleate solution, they found that 0.22 M NaCl and 0.24 M Na_2SO_4 are necessary to precipitate an oil emulsion and separate it into two layers. It will be seen that if the concentration of these electrolytes are expressed in equivalents far greater quantities of Na_2SO_4 are required to precipitate the emulsion than NaCl, which points to the fact that anions have a marked effect on the precipitation of the negatively charged emulsions. They have also studied the inversion of oil-in-water emulsion to water-in-oil emulsion by various electrolytes. Aqueous solutions of $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$ and $FeCl_3$ were used. With magnesium salts no absolutely sharp inversion point was found, but, rather, a time-period of instability during which inversion took place. Complete inversion took place with trivalent electrolytes. This shows that the trivalent cations are more effective precipitants and invertors of type than Mg; consequently, more magnesium salts are necessary to bring about the inversion in the type of the emulsion.

The first effect observed on adding a magnesium salt was to lower the viscosity of the oil-in-water emulsion. This was followed by an increase in viscosity, with oil appearing as the external phase. The initial drop in the viscosity of the oil emulsion can be attributed to the adsorption of ions carrying the same charge as the emulsion and consequent increase in the degree of dispersion. In a recent paper Dhar has emphasised that, keeping other variables constant, the increase in charge on suspended particles in water results in the partial dehydration so that there is a fall in viscosity which is intimately connected with the amount of bound and free water. Such initial drop in the viscosity on the addition of small quantities of electrolytes like NaOH, KCl and NaCl to sodium palmitate solution has been observed by Farrow.[1] On the addition of more electrolyte the viscosity increases very rapidly. More or less similar results have been obtained by Woudstra[2] with $Fe(OH)_3$ sol, though less markedly. It has been observed by Clowes that chloride ions are appreciably adsorbed by soap films from NaCl solution and McBain and Salmon[3] have also observed that both Cl′ and OH′ ions are adsorbed by soap. The increase in viscosity is certainly due to the coagulation of the sol with the increasing concentration of the electrolyte and the subsequent abstraction of the free water by the coagulam. It is therefore, clear that an increase in viscosity on the addition of magnesium salts to 'Nujol' emulsion is due to the dispersion of water-in-oil medium and this can be compared with a jelly of the so called 'hydrophile colloids' in which water is dispersed in the solid medium.

---

[1] "Margarine," 72 (1920).

[2] Chem. Met. Eng. **22**, 1061 (1920).

[3] U. S. Bur. Standards, Tech. Papers No. **86**, 17 (1917).

[4] J. Ind. Eng. Chem. **13**, 1009 (1921).

[5] "Petroleum," **19**, 611 (1923).

[6] Science, **59**, 463 (1924).

[7] J. Ind. Eng. Chem. **13**, 1119 (1921).

Bhatnagar[4] has made several experiments on the inversion of the two types of emulsion by electrolytes. It has been observed by him that the greater the concentration of KOH the greater is the amount of $Ba(NO_3)_2$ required to complete the inversion. On plotting a graph with his results, it is found that the Freundlich exponential adsorption formula is strictly followed as has been already shown with the results obtained by Clowes. Bhatnagar has got the following order Al > Cr > Ni > Pb > Ba > Sr, Ca, Mg beginning with the cation possessing the greatest influence on the inversion of phase. The coagulating power of these cations with As_2S_3 sol as obtained by Linder and Picton[5] is in the order Al > Pb > Ba > Sr > Ca, Mg > Ni beginning with the cations possessing the highest coagulating power.

It will be interesting here to consider some results of Bhatnagar[6] on the effect of dilution towards the inversion of the type of emulsion by different electrolytes with a paraffin-in-water emulsion.

Amount of sodium oleate in each sample = 0.101 millimole

20 cc emulsion	$BaCl_2$ in millimole at the inversion point	$Al_2(SO_4)_3$ in millimole at the inversion point
Standard emulsion.	0.050	0.015
" (twice diluted)	0.0798	0.025
" (thrice diluted)	0.112	0.040
" (four times diluted)	0.156	0.057

---

[1] J. Chem. Soc. **101**, 347 (1912).
[2] Kolloid-Z. **8**, 73 (1911).
[3] J. Chem. Soc. **119**, 1369, 1374, 1669 (1921).
[4] J. Chem. Soc. **119**, 61, 1760 (1921).
[5] Burton: "Physical Properties of Colloid Solutions," 158-160 (1920).
[6] J. Chem. Soc. **119**, 61, 1760 (1921).

The results in the above table indicate that greater the dilution of the emulsion the greater is the concentration of the electrolytes necessary to bring about an inversion in phase. The most striking point observed in these results is that more abnormality is observed with $Al^{\cdot\cdot\cdot}$ ion than with $Ba^{\cdot\cdot}$ ion. The concentration of $BaCl_2$ required to invert the phase of four times diluted emulsion is about three times the concentration of $BaCl_2$ required to invert the strongest emulsion, whilst the concentration of $Al_2(SO_4)_3$ required to invert the phase of the diluted emulsion is about four times the concentration of $Al_2(SO_4)_3$ required to invert the strongest emulsion. This peculiar behaviour of $Al^{\cdot\cdot\cdot}$ ion cannot be easily explained from the point of view that the stability of a sol entirely depends upon the increase in distance between the particles on dilution. This view advanced by Kruyt and Spek,[1] Mukherji and coworkers[2] and others indicates that the effect will be more marked with $K^{\cdot}$ ion, less with $Ba^{\cdot\cdot\cdot}$ ion, and still less with trivalent $Al^{\cdot\cdot\cdot}$ ion. Kruyt and Spek, Burton and Bishop[3] and others have observed that on diluting a collodial solution more of uni-valent salts like KCl, NaCl, etc., are necessary to coagulate a dilute sol than a concentrated one and the amount of tervalent ions from salts like $AlCl_3$, $CrCl_3$, required to coagulate a sol decreases with the decreasing concentration of these electrolytes, whilst practically constant amounts of such salts as $BaCl_2$, $SrCl_2$, etc., are necessary to coagulate a strong or a dilute sol.

We are of the opinion that the results of Bhatnagar do not support the view that the stability of an emulsion is due to an increase in the distance between the dispersed particles. The following explanation, which is based on the assumption that the abnormal dilution effect, i.e. more of an electrolyte is necessary to coagulate a dilute sol or emulsion than a concentrated one is a direct consequence of the adsorption of an ion carrying the same charge as the sol or emulsion, can satisfactorily explain the behaviour of $Ba^{\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ ion. When an electrolyte say AB is added to a sol or an emulsion carrying a negative charge, it is well known that if it can adsorb the anion B' carrying the same charge as the sol or emulsion appreciably, it will tend to increase the stability of the sol or emulsion and the process will follow the ordinary adsorption law. Now, if the sol is diluted twice, it is well known that the amount of adsorption of the anion B' is always greater than half the amount of adsorption by the concentrated sol or emulsion, consequently the amount of adsorption of anion B' adsorbed by an unit mass of the suspended matter is greater for the dilute sol or emulsion than the concentrated one. The dilute sol or emulsion is, therefore, stabilised to a greater extent than the concentrated one due to the greater adsorption of anion B'. Hence, more of an electrolyte is necessary to coagulate a dilute sol than a concentrated one in the presence of AB if the anion B' is appreciably adsorbed and stabilises the sol.

The following experiments with silver sol prepared by Kohlschütter's method will show that more abnormality is observed in the presence of an alkali. It is well known that AgOH is not completely decomposed by hydrogen and free OH ion is always present, which peptises the sol.

---

[1] Kolloid-Z. **25**, 3 (1919).

[3] J. Chem. Soc. **115**, 461 (1919).

[2] J. Phys. Chem. **24**, 701 (1920).

Concentration of the sol = 0.08 grm of Ag per litre Sol A = 4 cc made up to 8 cc; volume = 8 cc.

Immediate change in colour is observed.

Concentration of the sol.	KNO_3 N/8 c.c.	KNO_3 N/8 in presence of 0.1 c.c. NaOH N/5.
A	0.8	1.2
3A/4	0.9	1.4
A/2	1.0	2.10

From this table it will be seen that the amount of KNO_3 required to coagulate the sol increases with the decreasing concentration of the sol, but the phenomenon is more marked in the presence of NaOH which is known to stabilise the sol in small quantities.

It has already been observed that in the presence of KCl, KNO_3, etc., more $BaCl_2$ or $AlCl_3$ is necessary to coagulate the sol of As_2S_3. This antagonistic effect of KCl towards $BaCl_2$ has been ascribed by us to the adsorption of chloride ions carrying the same charge as the sol from KCl. It has been already shown that more of chloride ions are adsorbed by a dilute sol than a concentrated one; consequently, the antagonistic effect of KCl towards $BaCl_2$ or $AlCl_3$ will be more marked with a diluted sol of As_2S_3 than a concentrated one. This has been already shown by Sen[1] that the antagonistic effect of NaCl towards $CaCl_2$ is more marked for the dilute sol than the concentrated one.

We have already cited in this paper that NaOH or soap exert an antagonistic effect on the inversion of an oil emulsion by $Ba(NO_3)_2$. Briggs[2] has shown that soaps are markedly adsorbed by benzene-water interface and it is clear that this adsorption will be more marked when the emulsion is diluted; consequently, more marked antagonism will be observed with a diluted emulsion than a concentrated one, so that more of an electrolyte is necessary to invert a dilute emulsion than a concentrated one.

The abnormal behaviour of $Al^{\cdots}$ ion towards the coagulation of aniline emulsion is more due to the peptising effect of OH' ion obtained from the dissolved aniline than due to the adsorption of the ion carrying the same charge as the emulsion from $Al_2(SO_4)_3$ because the concentration of SO''_4 ion is very small. Now, when an aniline emulsion is diluted the amount of OH' ions in a given volume of the emulsion increases because more of aniline dissolves due to an increase in the amount of water phase. It is well known that OH' ions stabilise a negatively charged emulsion and the phenomenon is more marked with a diluted sol than the concentrated one. This is the probable explanation of the abnormal behaviour of $Al^{\cdots}$ towards dilution of aniline emulsion as observed by Bhatnagar.

[1] Private communication.

[2] J. Phys. Chem. **19**, 210 (1915).

Bhatnagar has studied the effect of various soap solutions on the stability of paraffin oil emulsions and his results indicates that soaps can be arranged in order of their protective effect. It is found from his results that the stability of the emulsion increases with the increase in the concentration of the added soap and that on allowing for experimental errors straight lines are obtained when the logarithims of the concentrations of the soap solution are plotted as ordinates and the logarithims of the corresponding of amounts of the electrolytes required to bring about the inversion as obscissae.

This shows that here we are dealing with the pure adsorption phenomenon and subsequent stabilisation due to the adsorption of the highly colloidal soap micelles. It will be interesting at this stage to describe the experimental results of Briggs on the adsorption of soap in the interface between benzene and water. Briggs has shown that the amount of soap adsorbed agrees fairly well with Freundlich's adsorption formula. It is, therefore, certain that the formation of an oil-in-water emulsion depends upon the adsorption of the highly charged soap micelles, just as $Fe(OH)_3$ is peptised to a colloidal solution by an acid due to the preferential adsorption of hydrogen ions. The greater peptising effect of a soap solution than that of an alkali is due to the colloidal nature of soap. It has been shown by us[1] that an adsorbent like $BaSO_4$ can adsorb colloids in greater quantities than molecules or ions from molecular solutions.

In a recent paper Seifriz[2] has studied the reversibility of hydrocarbon oil emulsions prepared from hydrocarbons of varying densities. It has been shown that heavier petroleum oils form water-in-oil emulsion in the presence of casein. The author has observed that the relative potency of ions in their ability to reverse the stable water in oil type to oil in water type is in the order $Na(OH) > Ba(OH)_2 > Th(NO_3)_4 > Al_2(SO_4)_3$, whilst NaCl and $BaCl_2$ cannot reverse the type at all. Seifriz concludes from these results that there is nothing to suggest the effect of valency of electrolytes on emulsions. On careful consideration we find that the above order of the electrolytes is quite reasonable as will be evident from the following point of view:

It is well known that the stability of a suspensoid or an emulsion is chiefly due to the electric charge on the suspended particles. It is, evident that the greater inverting influence of either NaOH or $Th(NO_3)_4$ is certainly due to the marked adsorption of OH' or of polyvalent $Th^{\cdot\cdot\cdot\cdot}$ ions by the particles of oil. The experiments of Powis in which he has shown that $Th^{\cdot\cdot\cdot\cdot}$ ions can reverse the charge of oil globules has been already cited. NaCl and $BaCl_2$ on the other hand possess no marked inverting effect because chloride ions are not so markedly adsorbed as OH' ions and the other cations are also not as effective as $Th^{\cdot\cdot\cdot\cdot}$ ion. It is quite probable that the oil-in-water emulsion obtained with an hydroxide is negatively charged and that obtained with $Th(NO_3)_4$ or $Al_2(SO_4)_3$ is a positively charged emulsion.

---

[1] Compare Ghosh and Dhar: Kolloid-Z. **35**, 144 (1924).

[2] J. Phys. Chem. **39**, 587 (1925).

Summary

1. It is shown that an oil emulsion closely resembles a colloidal suspension and the generalisations advanced for a sol is followed by an emulsion.

2. The separation of oil-in-water emulsion into two layers can be regarded as the coagulation of the dispersed oil globules. The reversal of phase of oil-in-water is probably the dispersion of water particles carrying a positive charge in the oil.

3. From the experimental results of various workers it is concluded that salts like NaCl, KCl, Na citrate, NaOH, etc., favour the formation of an emulsion of the type oil-in-water. This shows that anions viz, Cl′, Cit‴, OH′, etc., are appreciably adsorbed by the oil globules.

4. It has been deduced that the adsorption of the anions is mainly responsible for the antagonism observed between the electrolytes of monovalent cations like NaCl, KCl, NaOH, etc., towards salts of bivalent and trivalent cations like $Ba(NO_3)_2$ $AlCl_3$, $Al_2(SO_4)_3$, etc., on the inversion of an oil emulsion.

5. It is shown that the (a) abnormal dilution effect i.e. more of an electrolyte is necessary to coagulate a dilute emulsion than a concentrated one and (b) the antagonistic effects observed between salts of monovalent cations and bivalent cations on the inversion of the types of the emulsion are essentially connected and go hand in hand. This generalisation has already been advanced by us in a series of papers for ordinary sols.

6. It has been emphasised that the stability of an oil emulsion in the presence of soaps mainly depends on the electric charge of highly adsorbed soap micelles.

Chemical Laboratory,
University of Allahabad,
Allahabad, India.
June 24, 1925.

GEL STRUCTURE*

BY WILLIAM C. ARSEM

Introduction

Gels are of very common occurrence and of great importance biologically and technically. Practically all the tissues of living matter have gel structure, and the study of the behavior and properties of typical animal and plant gel-forming substances is assuming ever increasing importance.

Gel phenomena occur in the great industries of soap, leather, rubber, celluloid, paint, varnish, textiles, bread, glass, lubricants, photography and many others. Important problems of these industries are related to the swelling and shrinkage of gels, and their reversible or irreversible transformations into other states of aggregation.

Historical

There still exists considerable disagreement as to the number and relationship of the phases in a gel. Many writers appear still to hold the view that a gel is a homogeneous system. The evidence for this view is discussed by Katz.[1] Other investigators consider a gel to be a heterogeneous system composed of two mingled phases, either liquid-liquid or solid-liquid. Wo. Ostwald held that a gel was made up of two liquid phases, but this view now seems untenable. No two-phase emulsion is known which has the properties of a gel. Hatschek[2] has shown mathematically that the elastic properties of gels are not easily accounted for by this type of structure. The two-phase solid-liquid theory is very old, and many variants of it have been advanced. Thus various writers have pictured the solid phase as having a honeycomb, network, sponge or fibrillar structure.

Bütschli (1902) tried to render gel structure visible by the microscope, and described a foam-like appearance which is presumed by others to have been simply an optical effect. Ultramicroscopic study beginning with the work of Zsigmondy (1912) has shown that many gels are apparently without structure, but that in some cases where structure is seen, the solid phase is not a honeycomb, but a mass of straight fibrils intersecting and joined at their points of intersection. This structure has been observed in gels of soap, barium malonate and fibrin.

J. O. W. Barratt[3] has shown that fibrils in a solution of fibrinogen can be made to increase by growth at the expense of the liquid until a diameter of 1 μ has been reached. On the other hand all gels which show a structure under the ultramicroscope are not fibrillar. Gelatine and cellulose appear to consist of minute portions joined in a somewhat irregular manner according to Harrison[1] who photographed them with a Zeiss cardioid condenser using direct sunlight. The fibrils in soap gels are probably crystalline. Gelatinous crystals can also be observed in the gels obtained from concentrated solutions of benzopurpurine and chrysophenine. (Harrison[1]).

---

*Read at Milwaukee meeting of American Chemical Society Sept. 1923.

[1] Kolloidchem. Beihefte, **9**, 1-182, (1917).

[2] Trans. Faraday Soc. **12**, 17 (1917).

[3] Trans. Faraday Soc. **16** appendix, p. 49, (1920-1921).

Evidences of slow crystallization in gelatin gels and silica gels have been observed by S. C. Bradford[2]. Zsigmondy[3] believed that silica gel had an extremely fine porous structure with amicroscopic pores. The adsorption and drying isotherms of silica gel in presence of water, alcohol and benzene were studied by J. S. Anderson[4] who considered that his results might seem to indicate the existence of pores with a diameter of 2.62 to 5.55 $\mu\mu$.

The Nature of Gels

The view which I wish to present is as follows:

A normal gel consists of two phases which may be distinguished and designated as

a. The associated phase
b. The free phase

The associated phase is a single large molecule having the same shape and volume as the entire mass of the gel. It is made up of molecular units held in combination by the same kind of forces as those which function in the formation of a crystal lattice. (The term "molecular unit" is used for the grouping of atoms corresponding to the empirical formula. For example, NaCl is the molecular unit from which the large molecule or crystal $(NaCl)_n$ is built up, and SiO_2 is the molecular unit of the associated phase of silica gel.) These forces are, in fact, the residual valences of the molecular units. The associated phase differs from a normal crystal lattice in that the molecular units are irregularly oriented, only a fraction of the residual valences are employed in holding the structure together, and the lattice is, in consequence, much expanded and contains an extremely large number of voids of approximately molecular unit dimensions. The associated phase is thus conceived as an attenuated or expanded solid.

The free phase permeates the associated phase and fills the voids in it. In special cases, molecules of the free phase substance may take part in forming the lattice structure of the associated phase just as water does in hydrous crystals.

A normal gel may also be regarded as a uniformly porous, imperfect crystal filled with a fluid; or as an intimate mixture of two continuous phases, one solid, the other fluid, the solid phase being continuous in the special sense indicated.

Types of Gel

We may distinguish two types of gel, the special characteristics of which will be made clear in the discussion which follows.

---

[1] Trans. Faraday Soc. **16** appendix, p. 37, (1920-1921).

[2] Trans. Faraday Soc. **16** appendix, p. 56, (1920-1921).

[3] Z. anorg. Chem. **71**, 356 (1911).

[4] Z. physik. Chem. **88**, 191 (1914).

1. Normal gels, which have a uniform space distribution of the molecular units of the associated phase, with voids of approximately molecular dimensions.

2. Segregated gels, which have a non-uniform distribution of the units of the associated phase, which consequently has a relatively coarse structural framework in which the voids are much larger than molecular dimensions.

Effect of Progressive Association on a Dissolved or Dispersed Substance

The formation of crystals.

In a solution, the dissolved substance is completely dispersed in single molecular units or small aggregates having an association factor not far from unity. If the solution is saturated, and a change of condition is made which tends to cause separation of the solute, then progressive association of molecular units occurs through the union of residual valences. If conditions favor crystallization, normal crystal lattices are built up, and solid crystals result. This is especially true when concentration of the solution proceeds slowly, and its viscosity is low. Thus, R. W. Moore[1] was able to produce large perfect crystals of Rochelle salt by regulated cooling of a saturated solution. Such conditions favor the building of a perfect lattice, and large crystals tend to form.

If these conditions are departed from, there is a tendency toward irregular arrangement of the units in the building up of the lattice, the crystals are irregular, twinned, hopper-shaped, etc., and mother liquor is included. The inclusion of water in a crystal is some evidence of departure from the regular close-packed arrangement of atoms which is characteristic of a normal lattice, with the consequent formation of voids filled with liquid. A crystal containing included liquid may contain a certain proportion of gel structure.

The formation of gels.

In many cases when a substance separates from solution, conditions do not favor the building of a normal and regular crystalline lattice structure. This is especially true when the substance has a high molecular weight or great complexity, or when the solution from which it separates is greatly supersaturated. Many proteins, proteoses and carbohydrates form gels readily because their large and unsymmetrical molecular units do not orient themselves regularly upon separation from solution, so that an expanded lattice is built up with its units irregularly arranged and not closely packed.

When a normally insoluble substance like SiO_2, Fe_2O_3, $Al(OH)_3$, etc. is produced by a chemical reaction the velocity of separation from the supersaturated solution may prevent regular orientation and cause gel formation.

Irreversible Changes in the Solid Phase

Syneresis.

The structural arrangement of units in a gel is inherently unstable. A further condensation of the associated phase is possible through the re-orientation of units, the release of loosely combined molecules of the liquid phase, and the union of previously non-functioning residual valences. If complete re-orientation of all units is possible, the associated phase eventually becomes crystalline and the gel reverts to a mixture of crystals and free liquid. Syneresis may be defined as shrinkage of the solid phase caused by progressive association and re-orientation of molecular units.

---

[1] J. Am. Chem. Soc. 41, 1060 (1919).

Segregation.

The associated phase of a normal gel may undergo segregation instead of shrinkage. When this occurs, the molecular units may gather into groups, the configuration of which will depend on the structure of the units. Such substances as soaps with long chainlike molecules might be expected to segregate into threadlike groups and thus produce the fibrillar framework which has been observed. The elements of this framework, the fibrils themselves, may still have normal gel structure, which must necessarily be richer in associated phase than the original gel. If segregation continues, the framework may shrink still more and fracture at numerous places to make possible the formation of such aggregates as curds, clots and precipitates which are more concentrated than the original gel.

Reversible Changes in the Solid Phase

Stiffening and softening.

These changes in rigidity of the solid phase are due to changes in the proportion of free residual valences. They are essentially dissociation phenomena. A gel with a given concentration of associated phase may exist in a whole range of modifications characterized externally by different degrees of rigidity. This is because the proportion of residual valences of the solid phase substance which function as lattice-forming bonds may vary in accordance with the thermal history of the sample, and with the presence or absence in the free phase of substances capable of fixing these bonds, and thus preventing lattice formation. Such changes in rigidity may be brought about by temperature changes, H or OH ions, certain salts, dehydrating agents, and by mechanical means.

Reversible Changes involving both Phases

Swelling and shrinkage.

In order to explain the swelling process it is necessary to have some theory of the process of solution. When a crystalline substance goes into a true solution, it seems permissible to suppose that the lattice-forming residual valence bonds are separated and appropriated by the superior combining power of the solvent molecules, so that the crystal structure is entirely broken down and the molecules individually dispersed. In a gel, however, some of the residual valences function permanently as lattice bonds while others remain free and can hold or release molecules of free phase in accordance with surrounding conditions. Swelling, then, is the result of the combination of the molecules of a fluid with the free valences of a gel lattice.

The effect of hydrogen ion concentration on the degree of swelling of amphoteric gels like gelatin may be explained thus. On the acid side of the isoelectric point the amphoteric union of NH_2 and COOH is broken when the basic group is fixed by the anion of the added acid, leaving the equivalent amount of COOH free to take up water molecules, and vice-versa.

Relations and Transformations of Gel States

The associated phase may have all possible degrees of rigidity, and the gel may contain varying percentages of the free phase. In consequence, gels may exist with all degrees of rigidity from relative fluidity as in a cellulose nitrate solution, to high rigidity as in a glass, asphalt, or resin. Often a gel may be modified so as to have any desired rigidity by altering the proportions of the phases or by changing the temperature. Silica gel[1] exists in dilute forms which will flow, and in concentrated forms which are brittle and can be powdered. In cellulose nitrate "solutions" the fluidity decreases rapidly with increase of concentration and there is a definite yield value. The transition from viscous to plastic flow occurs at concentrations less than 1% according to work of W. L. Hyden quoted by Bingham.[2] On warming a solution of cellulose nitrate in acetone, the friction in terms of shearing force becomes zero at 43°C, so that above this temperature such solutions are true fluids, while below it they are soft solids.[3] Certain other gels probably have erroneously been considered to be sols because of their mobility. Such mobile gels still act like solids in many respects. For example, a hot 10% solution of gelatine can not be mixed with a hot 2% solution of agar.[4]

To make clear the relations of gel states as indicated by the lattice theory, we may consider the diagram:

$$\begin{tikzcd}
\begin{array}{c}\text{A-Dilute gel.}\\ \text{Low \% lattice.}\end{array} \arrow[r, shift left] \arrow[dd, shift right] & \begin{array}{c}\text{C-Concentrated gel,}\\ \text{Low \% lattice.}\end{array} \arrow[l, shift left] \arrow[dd, shift right] \arrow[dr] & \\
 & & \text{E-Crystals.} \\
\begin{array}{c}\text{B-Dilute gel,}\\ \text{High \% lattice.}\end{array} \arrow[r, shift left] \arrow[uu, shift right] & \begin{array}{c}\text{D-Concentrated gel,}\\ \text{High \% lattice.}\end{array} \arrow[l, shift left] \arrow[uu, shift right] \arrow[ur] &
\end{tikzcd}$$

Examples of these types are:

A. Warm dilute gelatin "solution". Most of lattice-forming bonds free, and gelatin in sol or solution state chiefly.

B. Cold dilute gelatin gel, completely set.

C. Warm concentrated gelatin "solution."

D. Cold concentrated gelatin gel, completely set.

The changes A $\rightleftarrows$ C and B $\rightleftarrows$ D are usually reversible, and involve both phases. They can be carried out by drying or swelling processes, and are accompanied by characteristic changes in rigidity. There is probably no change in the number of lattice-forming bonds. A familiar example is the drying or swelling of pieces of gelatin jelly by evaporation or absorption of water.

---

[1] Van Bemmelen: "Die Absorption", 196, 214, 232 (1910).

[2] "Fluidity and Plasticity", 291 (1922).

[3] Bingham: "Fluidity and Plasticity", 243 (1922).

[4] Beijerinck: Kolloid-Z. 7, 16 (1910).

The changes A ⇄ B and C ⇄ D are changes in the associated phase involving the number of lattice-forming bonds. They are reversible in some cases and not in others. As examples of reversible changes may be cited the effect of temperature changes on gelatin jellies, cellulose nitrate "solutions", asphalts, pitches, gums and resins.

The effects of temperature changes on gels bears an interesting relation to their effects on crystalline bodies. When a pure simple substance crystallizes by freezing, there is no gel structure in the liquid phase, and a sharp separation of solid from liquid occurs. When a melted gel is cooled, however, lattice structure begins to form throughout the mass long before the material as a whole becomes solid. This accounts for the indistinct melting point of a gel-forming substance.

Probable examples of irreversible changes A → B and C → D are: the coagulation of albumen by heat, the thickening of drying oils by heat, and the hardening of synthetic resins of the Bakelite type.

There are many examples of irreversible gel formation in which an additional reagent is involved, among which may be mentioned the vulcanization of rubber in which sulphur assists the formation of a gel lattice by linking the molecular units together; also the setting and drying of oils in paints and varnishes, in which oxygen plays a similar role.

By mechanical working, rubber can be depolymerized. In this way many of the residual valence unions of the lattice are broken by stresses which exceed the elastic limit, and thus the pseudo-solid associated phase of the gel is broken into smaller aggregates in the same way that an ordinary solid is pulverized by grinding.

An example of the change D → E is the devitrification of a glass. Another possible example is the crystallization of a metal or alloy under repeated stresses.

Schenectady, N. Y.

THE APPARENT VISCOSITY OF SOLUTIONS OF NITRO COTTON IN VARIOUS SOLVENTS

BY J. W. McBAIN, C. E. HARVEY, AND L. E. SMITH

The object of the present investigation, which has extended over the past six years, was to study all the factors which affect the viscosity of nitro cotton in various solvents with a view to testing the suggestion of H. Schwarz[1] that comparative fluidity is a criterion of solvent power—a suggestion which accords with the results of later workers and ourselves. The course of the investigation has increasingly emphasized the favorable effect upon solvent power of suitable admixtures so that frequently an ordinary specimen of solvent may owe a large part of its solvent power to impurity. The work has resulted in a definite theoretical conception of the processes operative in the formation of solutions and jellies of such substances as nitro cellulose.

The most important previous investigation was that of F. C. Baker[2]. Whereas Baker, probably relying upon the earlier work of C. Piest[3] had assumed that the viscosity of a solution of nitro cellulose in various solvents exhibited a definite value, A. M. Bakr and C. S. Salmon and R. D. Reid, in this laboratory in 1919, found that all the factors enumerated below affect viscosity. Thus, the viscosities previously recorded refer only to particular solutions of a given unspecified history, and change in conditions may alter their magnitude several fold.

We must emphasize at the outset that, if the technique of measurement is sufficiently standardized and the various factors suitably controlled, the apparent viscosity of a solution of nitro cotton is definite and the results are reproducible by different experimenters within a few per cent. The apparent viscosity is not a true viscosity because it is not independent of the rate of shear; nevertheless the value of the results is only slightly impaired by the fact that they are not universal constants but subject to correction when the conditions are widely varied. Such results will be shown to be both useful and significant.

Table of Contents

I. General experimental information on method, units and materials.
II. Factors which influence apparent viscosity of a sol of nitro cotton.
  1. Concentration.
  2. Temperature of measurement.
  3. Method, period and temperature of preliminary drying of nitro cotton.
  4. Previous mechancial treatment.

---

[1] Kolloid-Z., 12, 32-41 (1913); J. Soc. Chem. Ind., 32, 191 (1913).

[2] J. Chem. Soc., 103, 1653-1675 (1913).

[3] Z. angew. Chem., 24, 968-972 (1910).

5. Temperature of preparation of the solution.
6. Exposure to light.
7. Actual specimen of nitro cotton (nearly all the experiments here recorded refer to one specimen).
8. Purity of solvent; impurities and admixtures with other solvents and non-solvents.
9. Nature of solvent.
10. Degradation of nitro cotton.
11. Age of the solution.
12. Temperature of storage of solution.

III. Effect of preliminary treatment with acetone or aqueous acetone.
IV. Alcohol as a solvent.
V. Properties more or less parallel with solvent power.
VI. General Summary.
VII. General Conclusions.

I. General Experimental Information on Method, Units and Materials

a. Materials.

For most of the chemicals used we are indebted to Messrs. Nobel's Explosives Co., Ltd. In a number of cases, successive samples were supplied and more stringent precautions were taken in purifying them, so that in most cases our latest measurements refer to the purest obtainable materials. Increasing purity definitely impaired the solvent power of most of these solvents and greatly increased the viscosity of nitro cotton therein. Furthermore, it was found that, in keeping specimens of solvents for a few years, in most cases, the viscosity of solutions made from them became less, evidently through slight decomposition. A few of the solvents were procured from British Houses and a few from Kahlbaum, and one sample of diethyl phthalate from Eastman Kodak Co.

Table I gives a list of the solvents used and indicates the constants of the purest samples received from each source.

b. Preparation and storage of solutions.

There is no apparent limit to the concentrations of these solutions which can be made up, but above 10% they are quite solid.

The method of preparation of a solution greatly affects its whole subsequent history. For instance, even the order of mixing has its effect. When nitro cotton is placed in an empty tube and solvent added the nitro cotton (where wetted) almost instantaneously turns to a hard lump of jelly which frequently sticks obstinately to the glass, requiring long continued violent shaking to dislodge and dissolve it. For the same reason a narrow neck or corners must be avoided in the tube used for the preparation as they provide

TABLE I

Densities and viscosities of pure solvents used. (Temp. 55°C)

Chemical	Firm	Date supplied	Date measured	Density $D^{55°}_{4°}$	Viscosity (poises)
Acetone	Purified	1924	1924	0.7865	0.003039 (25°)
Acetophenone	Nobels	6/11/22	1924	1.000	0.0103
Benzophenone	Nobels	2/4/25	1925	1.081	0.04647
Benzophenone	Kahlbaum	1925	1925	1.081	0.04688
Benzyl formanilide	Nobels	16/2/25	1925	1.100	0.1163
Benzyl phenyl urethane	Nobels	12/3/24	1925	1.076	0.1096
Diethyl phthalate	Nobels	1923	1924	1.087	0.04184
Diethyl phthalate	Kodak	1925	1925	1.087	0.04180
Ethyl formanilide	Nobels	1924	1925	1.024	0.02418
Ethyl phenyl urethane	Nobels	1923	1924	1.013	0.02760
Formanilide	Nobels	1/5/24	1925	1.114	0.08794
Formanilide	B. D. H.	1924	1924	1.114	0.08624
Form-o-toluidide	Nobels	2/2/22	1924	1.086	0.1291
Methyl phenyl urethane	Nobels	8/8/23	1924	1.012	0.0255
Methyl cyanilide	Nobels	6/11/22	1924	1.040	0.02037
Methyl ethyl ketone	Purified	1924	1924	0.8013	0.004976 (25°)
Nitrobody	Nobels	1922	1922	1.392	0.0787
Ortho-tolyl urethane	Nobels	1924	1925	1.061	0.07425
Ortho-tolyl oxamic ester	Nobels	1922	1922	1.126	0.1566
Phenyl urethane	Nobels	1923	1925	1.085	0.8535
Phenoxyacetic ester	Nobels	1922	1924	1.071	0.0262
Triacetin	Nobels	1922	1925	1.119	0.04790
Triphenyl phosphate	Nobels	22/2/22	1922	1.202	0.0950

One sample of nitro cotton was used throughout. It was prepared by Messrs. Nobel's Explosive Co., Ltd. by the displacement process and supplied on March 27, 1919 and kept cold and wet in a dark stove. It had been freed from calcium carbonate, with acetic acid; nitrogen content 12.10% solubility in ether-alcohol 99.45%, ash 0.27%. Where not expressly stated it was dried for three hours at 60° though dried samples were often kept before use in a tightly stoppered bottle in a desiccator over phosphorus pentoxide at room temperature before use.

a lodgement for the half-dissolved gel. A great difference is noted in the behavior of good and poor solvents in the time taken for the viscid gel to disperse throughout the solution. An excellent solvent may do this in a few minutes, where, under the same conditions, a poor solvent may require a week or more.

Throughout the present work, tubes of practically the same diameter, 2 cms., were used, but the method of mixing the nitro cotton and the solvent was as follows:—

About 3 ccs of the solvent were first added to wet the lower half of the tube, and the nitro cotton weighed in by difference from a glass bulb of approximately 10 cc. capacity, fitted with a delivery tube about 6 cms. in length, so that no nitro cotton touched the inside of the tube which had not been wetted by the solvent. More solvent was then added to make up to the required strength, the tube sealed, and placed in the shaker at 55°C in the dark. In this way, the lump of gel formed is easily detached or comes away from the sides of the tube, and floats about in the solvent from the commencement of the shaking. One hour after ageing has commenced, the shaking is started and continued for 22 hours, when the tube is removed, opened and the sol filtered through a special sieve made from very fine gauze of pure silver, folded into four layers to eliminate any nitro-cotton impurities and fibres. The tube containing the filtered sol was covered with tin foil to prevent access of light, and after allowing it 15 minutes to acquire the temperature of the 60° electric oven, 5 ccs. each for the viscosity measurement and the preparation of the diluted solutions for the concentration curve at 24 hours age were extracted, and the tube, carefully sealed with a cork, was suspended in the 55° thermostat.

Since the time required for the production of homogeneous sols is greatly influenced by mechanical shaking, it is necessary that the "shaker" dimensions be known in order that the results may be reproduced at will. The essential dimensions for the shaker used as determined by Bennett are given in Table II.

TABLE II

The dimensions of the shaker

Length of shaker arm	41 cms.
Length of stroke (distance centre of tube moves)	6.8 cms.
Number of strokes per minute with one tube fixed	610-620 (single) 305-310 (double)

Two methods were used for diluting the solutions. In one case a small bottle was weighed empty, then a quantity of solution was added and again weighed, to this was added the requisite amount of solvent to make up to either 0.1% or 0.2% approximately. In the other case the storage tube itself was used instead of the bottle, thus doing away with the necessity of transference of the solution from the bottle to the tube. Latterly the second method was used almost entirely. In each case the dilution was carried out as quickly as possible, the solutions being well shaken and put in the thermostat without delay.

Sufficient original solution was made up, and sufficient diluted to last for several (at least five) viscosity determinations. It was thought to be an advantage to have solutions of exactly the same concentrations for successive ageings. All solutions were preserved in sealed tubes similar to those used in the preparation of the sols. After each determination of viscosity the solution was poured carefully from the viscometer into the ageing tube.

c. *Design of viscometers.*

The special designs of the accurate viscometers used for this work were based upon a study of the work of F. Baker[1], Grüneisen[2], Appleby[3], Washburn and Williams[4], and Bingham[5]; and were such that they obeyed Poiseuillle's law to within 0.1% accuracy when the time of flow was slightly greater than 200 seconds. Bungenberg de Jong[6] has also published a useful summary and discussion of this subject. The most convenient reference is British Eng. Standards Association, No. 188 (1923) "Determination of Viscosity in Absolute Units." The kinetic energy correction, which Bingham regards as highly important for absolute values, was made practically negligible by suitable design.

d. *Standardization of viscometer tubes.*

All viscometers were thoroughly cleaned with acetone before use, since this is the best solvent for the nitro cotton sols, and were then carefully dried with dust-free air and allowed to stand for 15 minutes in the 60° electric oven together with the calibrated pipette (made to deliver 5 ccs. at 55° to within 0.01 ccs). Two rubber tubes about 25 cm long were then attached to the two openings of the viscometer to prevent access of condensed vapor, the viscometer suspended in the 55° thermostat and securely held in a clamp so that the capillary limb appeared vertical when viewed from two directions at right angles. The viscometer was allowed 15 minutes to acquire the temperature of the thermostat before the time of flow of the liquid was measured. The temperature of the thermostat could be kept constant at 55° within 0.02°C. The correct value for the time of flow at 55.00° was obtained by interpolationg the times of flow and the various temperatures recorded.

Table III gives the values obtained for the viscometer constants by H. B. Bennett, P. R. Edwards and L. E. Smith together with the dimensions required for any kinetic energy correction. The repeated standardization was

---

[1] J. Chem. Soc., **103**, 1653 (1913).

[2] Wiss. Abh. phys. techn. Reichsanstalt, **4**, 151 (1904).

[3] J. Chem. Soc., **97**, 2000 (1910); **103**, 2167 (1913).

[4] J. Am. Chem. Soc., **35**, 738 (1913).

[5] "Fluidity and Plasticity," (1922).

[6] Rec. Trav. chim. **42**, 1-24 (1923).

Table III

Dimensions and constants of viscometer tubes at 55°C

Viscometer	Length of capillary (cm)	Volume of bulb (cc)	Tube constant					
			Bennett		Edwards		Smith	
			K	log K	K	log K	K	log K
1AG	13.0	3.24	24.05	$\bar{4}.3811$	24.00	$\bar{4}.3802$	24.00	$\bar{4}.3802$
2BG	13.0	3.24	24.80	$\bar{4}.3945$	25.23	$\bar{4}.4019$	25.23	$\bar{4}.4019$
3AG	13.0	3.24	48.16	$\bar{4}.6826$	—	—	—	—
I (rep)	6.3	1.5	57.18	$\bar{4}.752$	—	—	—	—
I	6.3	2.7	(51.89)	$\bar{4}.7151$	—	—	—	—
4AG	13.0	3.24	75.86	$\bar{4}.8800$	—	—	—	—
P	13.0	3.24	92.55	$\bar{4}.9663$	91.96	$\bar{4}.9636$	91.96	$\bar{4}.9636$
N	6.0	2.5	96.27	$\bar{4}.9835$	—	—	—	—
O	6.3	2.0	111.7	$\bar{3}.0480$	111.7	$\bar{3}.0480$	111.7	$\bar{4}.0480$
T	5.6	1.1	510.9	$\bar{3}$ 7084	—	—	—	—
R	6.6	1.56	—	—	18.29	$\bar{4}.2622$	18.29	$\bar{4}.2622$
V_2	7 0	3.5	—	—	61.25	$\bar{4}.7872$	—	—

based upon 60% sucrose supplied by Bureau of Standards, Washington, using Bingham and Jackman's value[1] at 55.0°. The concentration of all sucrose solutions was checked by a determination of their density.

II. Factors which influence Viscosity of a Sol of Nitro Cotton

1. *No accepted formula represents the dependence of viscosity upon concentration.*

As a first approximation, the logarithm of the viscosity of solutions of nitro cotton at 55° follows the Arrhenius rule in being proportional to the concentration. Our more careful work has been carried out with solutions seldom exceeding 1% and generally 0.5% and when the logarithm of the relative viscosity is plotted against the number of grams of nitro cotton per 100 grams solvent there is a distinct deviation from the straight line in that the more concentrated solutions are less than proportionately viscous. Since the solutions are so dilute this discrepancy cannot be obviated by plotting concentrations in true per cent nor can it be ascribed to errors of calibration, etc., since it invariably appears when one actual solution is repeatedly diluted and passed through the same viscometer tube.

The deviation is in the opposite direction from that observed in solutions of proteins which Arrhenius was able to explain away by ascribing it to hydration. Hatschek[2] has pointed out that F. Baker's curves[3] deviate from the straight-line Arrhenius formula, the deviation being in the same direction and of the same magnitude as in our work. Hatschek points out that graphs of viscosity slope for solutions of rubber may diverge from a straight line to an equal extent in either this or the opposite direction. The Arrhenius formula is therefore invalid and it is a merely empirical approximate rule. Bingham's suggested rule that the fluidity should be linearly proportional to the concentration is far more widely at variance with the facts as Bingham himself has shown. Mardles[1] likewise found no simple relation between either viscosity or fluidity and concentration.

---

[1] Bureau of Standards Bull. **14**, 83 (Table XV).

[2] Biochem. J., **10**, 325 (1916).

[3] J. Chem. Soc., **108**, 1653 (1913).

This real discrepancy introduces an unavoidable difficulty in comparing the slopes for different solvents or for different conditions. We have therefore arbitrarily taken the mean value of the slope for solutions up to 0.5%. It is this slope; that is, logarithm of the viscosity of the solution divided by that of the solvent, calculated per gram of nitro cotton in 100 grams solvent that is recorded as the representative value in each case.

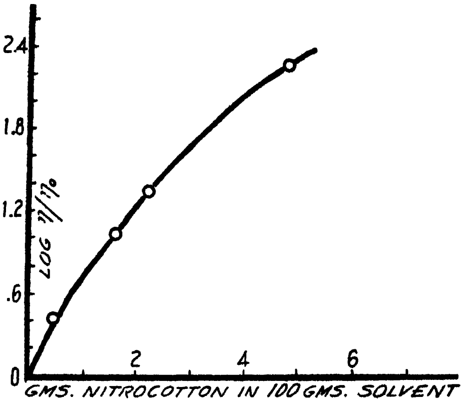


Fig. 1

Change with concentration of relative apparent viscosity of nitro cotton in ethyl formanilide at 55°.

It is difficult to dissolve large amounts of nitro cotton in the purer solvents now in use but Fig. 1 shows the results obtained by L. E. Smith using the latest technique for solutions up to 5% in one of the best available solvents, ethyl formanilide. This graph confirms all of the data obtained during the last few years with fresh solutions in that the curvature is undeniable. Solutions which have been allowed to age for long periods show viscosity much more nearly proportional to the concentration.

2. *The high temperature coefficient of viscosity.*

The viscosity of solutions of nitro cotton shows an extremely great temperature coefficient such as is found in the case of other gelatinising colloids, for example soap solutions. It is difficult to adduce a temperature coefficient which is not arbitrary owing to the interplay of the other factors under discussion but the magnitude of the effect may be illustrated by quoting W. A.

---

[1] J. Chem. Soc., **123**, 1951 (1923).

Squance's data for 0.4% solution of nitro cotton in ethyl phenyl urethane which at 30° is 0.368 and at 55° is 0.065; that is, a change of six-fold when the temperature is lowered only 25°.

3. *Method and period and temperature of preliminary drying of nitro cotton.*

In a paper entitled "Researches on Cellulose and its Ethers" II. 'The Stability and Viscosity of Nitrocelluloses' I, J. Duclaux[1] describes a series of experiments with 47 different varieties of nitrocellulose. The effect of heating the samples for various periods from 0-23 hours at temperatures of 100° to 110°C was measured by the loss in weight of the sample, and the resulting effect on the viscosity of the nitro cellulose solutions. Duclaux summarised his conclusions as follows:—

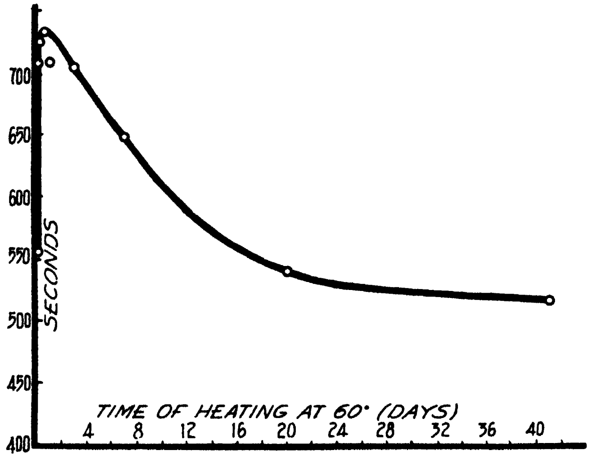


FIG. 2

Viscosity of solutions of 1 gram nitro cotton in 100 cc ethyl formanilide at age 24 hours at 55°; made from nitro cotton heated to 60° for various periods (the pure solvent about 100 seconds).

1. When nitrocellulose is heated, the viscosity of its solutions diminishes. This fall in viscosity is an absolutely general fact.

2. There is a direct relation between the fall in viscosity and the loss of weight of the nitrocellulose. In practice, the knowledge of one of these two quantities is sufficient to determine the other.

3. The study of the variations in the viscosity of a nitrocellulose during a prolonged heat treatment gives a very good method of following the degradation of that nitrocellulose and consequently of determining its stability.

4. This method of determining the stability, depending on viscosity measurements, offers important advantages over the current methods and does not appear to be inferior to them from the standpoint of sensitiveness.

Duclaux's treatment was however very drastic and nitro cotton can be maintained at 60° for long periods without appreciable loss of weight.

---

[1] Bull., 29, 374 (1921).

L. E. Smith has recently carried out a series of measurements using ethyl formanilide as solvent. The nitro cotton was heated in an electric oven at 60° for 41 days and from time to time specimens were removed and made up by weighing one gram of the nitro cotton into 100 cc of ethyl formanilide the solutions being prepared and measured in the usual way at 55° at age 24 hours. The results are given in Table IV and Fig. 2 and show a maximum viscosity when the nitro cotton has been heated about 12 hours falling off at about 70% of the maximum value in 41 days.

TABLE IV

Relation between viscosity of solutions of nitro cotton and the time of previous drying at 60°

Amt. of heating at 60°C (hours)	Age of solution (hours)	Time of flow (seconds)
1	24.1	556.6
3	24.1	707.9
7	24.0	724.6
12	24.0	734.0
24	24.0	(709.0)
3 days	24.1	704.6
7	24.0	647.8
20	23.9	539.8
41	24.1	517.4

A result obtained by P. R. Edwards for a sample of nitro cotton dried in a vacuum of 10 mm. mercury over phosphorus pentoxide for ten days at room temperature shows that nitro cotton can be dried effectually without heating.

4. *Violent shaking during solution greatly diminishes the viscosity.*

The dependence of viscosity on previous mechancial treatment is a commonplace in colloid chemistry particularly in the two cases of gelatinising sols and of sols which have been prepared by the swelling of colloidal material. It is the second case with which we are dealing here and it would be readily intelligible if the degree to which the structure of the fibres of nitro cotton is broken down were to depend on the intensity of the mechanical disintegrating forces applied. It would appear quite possible for nitro cotton to swell to an almost indefinite size in a suitable solvent without being disintegrated; that is, whilst still retaining certain bonds of union throughout, just as a starch granule may swell in the water to an enormous bulk and still retain some trace of its original structure.

Bakr, Salmon and Reid carried out experiments in this connection, using ethyl phenyl urethane and methyl phenyl urethane which showed that if nitro cotton were dissolved with very gentle stirring such as mere tilting of the solution from end to end of the tube, that its viscosity was twice as great as if placed for 2 hours in a shaking machine with moderate shaking even though the comparison was carried out a week afterwards.

Most of our experiments involve violent shaking until the solution is homogeneous and thereafter a comparison is made between solutions which are subjected to a continuation of the same shaking and those which are merely allowed to rest. The results in Table V show quite clearly that the prolongation of this thorough shaking produces no further effect.

TABLE V

Effect of continuation of standard shaking beyond the time of complete solution at 55°

Time shaken	Time of standing	Age measured	Concn. %	Viscosity slope
		Benzophenone. (Edwards)		
24 hours	0 hours	24 hours	0.3445	1.636
5¾	8½	24	0.4308	1.590
		Methyl phenyl urethane (Smith)		
4	20	24	0.4119	1.766
20	32	23.2	0.3761	1.861
23	1	24	various	1.879
20	27.6	47.6	0.3761	(1.775)
40	8.6	48.6	0.3761	(1.781)
		Phenyl urethane (Smith)		
24	23	47	0.3811	(1.655)
46.5	2.3	48.8	0.3811	(1.659)

Smith has recently carried out experiments which test directly the observations of Bakr, Salmon and Reid. Two kinds of shaking were compared; namely, standard shaking and mere tilting of the tubes back and forth once a second at right angles to their axes, Table VI.

TABLE VI

Effect on viscosity at 55° of slow tilting followed by rapid shaking

Time of tilting	Time of shaking	Time of flow
	Ethyl phenyl urethane	
3 days	None	542.4 seconds.
”	½ hour	390.4
3 days	none	152.2
”	½ hour	132.4
7 days	none	843.2
”	1 hour	837.0
	Ethyl phthalate	
3 days	none	118.0
”	½ hour	116.8

The time taken to prepare a homogeneous sol for a good gelatinizer and mild shaking is about 1½ days at 90° and 4 or 5 days at 55°; or, with violent agitation, 1½ hours at 90°, and 4 hours at 55°.

It is quite clear that vigorous mechanical treatment diminishes the viscosity of solutions of nitro cotton at 55° presumably by breaking down residual structure derived from the original fibres. However, if any definite treatment has been applied until it was certain that solution was complete, a further continuation of treatment not more violent has but a negligible effect. Again, violent treatment has its greatest effect at the beginning when the grossest aggregates are being broken up; if applied at a much later period it has comparatively little effect.

5. *The higher the temperature of preparation the lower the viscosity.*

The difference between solutions prepared at say 55° and 90° persists indefinitely showing no signs of disappearing even after a lapse of months. Owing to the fact that the best solvents dissolve nitro cotton so much more quickly than the worst ones it is sometimes possible to prepare solutions in good solvents with a slightly higher viscosity than bad solvents which have taken longer to prepare.

6. *Exposure to light distinctly diminishes the viscosity.*

It was shown in a previous report that light has the effect of slightly decreasing the viscosity of a solution of nitro cotton, the effect depending on the solvent and possibly the concentration of the nitro cotton. The effect is only a few per cent in diffused daylight. Throughout the present work solutions were prepared and kept in the dark. G. W. MacDonald[1] found that 2½% solution of nitro cotton in acetone fell off in viscosity to about half value on exposing the solution for seven days to the diffused light of the laboratory; whereas there was only a slight decrease on keeping the solution in the dark for seven weeks (at room temperature).

Exposure to ultraviolet light is said to increase solvent power of liquids. L. E. Smith found that a suspension of nitro cotton in alcohol is yellowed and decomposed with the result of partial solution. It seems probable that nitration of the solvent combined with denitration of the nitro cotton produces the enhanced solubility.

7. *Unrelated specimens of nitro cotton of similar chemical composition give solutions of very different viscosity.*

It is hardly necessary to quote experimental data in support of the foregoing statement but its significance lies in the clear indication given of the primary importance of physical state, structure and degree of subdivision, not only in the dry state but in the solutions themselves.

8. *Purity of solvent; impurities and admixtures with other solvents.*

(*a*) *Introduction.*

F. Sproxton[2] in summarising work on cellulose esters pointed out that up to 1920 no published investigation was available to show for any binary mixture what the optimum proportions are for maximum solvent power and minimum viscosity. He mentions well known qualitative instances of mixtures which are superior in solvent power to either constituent; such as ether-alcohol, and methyl alcohol containing traces of acetone. Piest in 1910 noted that addition of acetic acid to acetone or to ether-alcohol solution of nitro cotton diminishes their viscosity. By estimating the amount of low nitrogen nitro cotton dissolved by mixtures of alcohol with toluene Sproxton concluded that the optimum mixture in this case has the empirical composition $C_7H_8 . 3C_2H_5OH$. The position of this optimum remains unaltered if petroleum spirit is added but the solvent power is steadily decreased. Unlike alcohol, the solvent power of acetone is not enhanced even initially but only diminished by addition of toluene. Using cellulose acetate, mixtures of (non-solvent) alcohol with (non-solvent) n-tetrachlorethane containing 20-60% of alcohol are good solvents. Other similar instances of non-solvents of cellulose acetate which on mixing produce a solvent are cited (possibly from the work of Mardles, Moses and Willstrop) in an article in Chem. Trade Journ. 1923, 10th August, 155-157; thus chloroform and alcohol, ethyl acetate and benzyl alcohol above 40%; similarly "binary mixtures of esters and alcohols including water." Chandelon[1] observed that moist nitro cotton dissolves more readily than dry nitro cotton in ether-alcohol.

---

[1] J. Soc. Chem. Ind., **30**, 785 (1911).

[2] "Third Colloid Report", 84 (1920); Trans. Faraday Soc., **16**, Colloid Discussion 72-75 (1921).

The first systematic study was published by Gibson and McCall[2] using ether-alcohol (92% alcohol, 8% water) with different varieties of nitro cotton. They found an optimum proportion of ether and alcohol at which the viscosity was a minimum. This optimum was independent of the concentration of nitro cotton but it does depend to some extent upon the nitrogen content of the nitro cotton. As in our work, definite reproducible values for viscosity were obtained with a given sample of nitro cotton; but these were greatly dependent upon the origin and treatment of the nitro cotton. The optimum concentration of ether-alcohol solvent was not affected by addition of amyl acetate but the latter acts as a diluent or non-solvent and increases the viscosity. Masson and McCall[3] found an optimum solvent for nitro cotton when water is added to acetone, although if more than 12% of water was present the nitro cotton no longer dissolved.

Anna von Fischer[4] (working with Schwartz) used 30 cellulose acetates of 7 different types. The chief experiments were with alcohol-acetone as solvent. The optimum solvent for all good industrial cellulose acetates was 80% acetone-20% alcohol by volume, and the actual value of the minimum was very like for all cases. One however showed minimum viscosity in 70% acetone and one was insoluble in pure acetone. Almost all the technically useless cellulose acetates showed a very high viscosity in 70% acetone and exhibited a minimum in 90% acetone, but in general the minimum was much higher than that for good acetates.

---

[1] Bull. Soc. chim. Belg., **26**, 495-506 (1912).
[2] J. Soc. Chem. Ind., **39**, 172-176T (1920).
[3] J. Chem. Soc., **117**, 819-23 (1920).
[4] Kolloid-Z., **29**, 260-5 (1921).

Addition of 20% and 40% of camphor to pure acetone as solvent always increased the viscosity of the acetate solution and lessened its solubility. Cellulose acetate dissolves very much more readily in acetone to which 10% of triacetin has been added although the absolute viscosity is raised; no data are given for the solvents to enable any conclusion to be drawn as to whether the *relative* viscosity referred to the viscosity of the solvent is raised or lowered. Addition of dichlorhydrin to acetone causes the viscosity of solutions of cellulose acetate to pass through a minimum in some cases. p-Toluene sulphamide in some instances raised, in others lowered, the viscosity. The behavior is so closely linked up with that discussed in the preceding part of the paper that it might possibly be utilized as a factory test of the suitability of various cellulose acetates for the manufacture of celluloid. Turning to nitro cotton (10.4 to 10.6% N_2) it was found that nitro cotton suitable for celluloid manufacture showed in alcoholic solution containing two or more grams of nitro cotton a diminished viscosity upon addition of camphor; whereas bad nitro cotton gave solutions whose viscosity was progressively increased by addition of camphor.

Barr and Bircumshaw[1] studied the viscosity of cellulose acetate in 5% solution in pure acetone and in acetone to which water, benzene or alcohol was added in various proportions up to the amount that caused precipitation. Benzene causes a progressive increase in the viscosity whereas addition of water or alcohol gives an initial rapid fall in viscosity, which in the case of water reaches a minimum and then rises fairly rapidly, but with alcohol remains fairly constant at the low value.

Mardles, Moses and Willstrop[2] note that water up to 6% increases the solvent power of acetone for cellulose acetate. Minima in the viscosity of solutions of cellulose acetate in binary mixtures of alcohol with a second solvent were observed with tetrachlorethane, butyl formate, methyl benzoate, nitro xylol, etc., but the optimum mixture varied in composition for different varieties of acetate. No minima were produced by the addition of the pronounced non- solvent hexane to other solvents; whereas the mild non-solvent benzene and alcohol gave minima with benzyl alcohol. The higher the substance in any homologous series the less was the tendency to produce optimum mixtures.

In 27 mixtures of solvents for which curves are drawn in a later paper by Mardles[3] all but three show optima. However, a remarkably different behavior is said to be shown by mixtures of acetone and aniline, which separately are each solvents for cellulose acetate, whereas the mixture in the proportion of 1 mol aniline to 2 mols acetic acid does not dissolve cellulose acetate. For the present purpose we may quote only the results for nitro cotton where optima were obtained with alcohol-benzyl ethyl ether, and with alcohol-aceto-phenone, and with alcohol-acetone (and even with acetone to which was added a mixture of equal parts of alcohol and benzene). Several instances are given where a mixture of three non-solvents is required to dissolve cellulose acetate.

---

[1] Trans. Faraday Soc., **16**, Colloid Discussion, 72-75 (1916).

[2] Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.

[3] J. Soc. Chem. Ind., **42**, 129T (1923).

A further paper by Mardles[1] includes data for nitro cotton with acetone-water, and acetone-alcohol. A table of all binary mixtures hitherto studied with nitro cotton is given in the discussion below.

To sum up, in the great majority of cases, small additions of a second substance enhance the solvent power of a solvent for cellulose esters, as is shown by lowered relative viscosity or increased power of withstanding the precipitating effect of an extreme non-solvent such as petroleum spirit.

(*b*) *Viscosity data in binary mixtures of solvents.*

(1) Acetone-water at 25°C (Edwards)

Methyl ethyl ketone-water at 25°C (Edwards)

The above solvents were used in making solutions of nitro cotton under standard conditions at 55°C though the viscosity was measured at 25.00° (corrected). The results are recorded in Tables VII and VIII. In each case there is an optimum mixture at which not only the absolute viscosity of the solutions of nitro cotton but also the slope of the log viscosity is a minimum. 20% aqueous acetone did not dissolve nitro cotton at 55°C.

TABLE VII

Viscosity of nitro cotton sols in dry acetone and in acetone-water mixtures

(Sols shaken for 22 hours at 55.0°C measured at 25.00° in the dark)

Concn. water %	Concn. N.C. %	$d^{55°}_{4°}$ of sol gms./cc.	Age hours	η poises	log η	slope $\frac{\log \eta/\eta_0}{\text{concn.}}$
0.00	0.000	0.7865	—	0.003039	$\bar{3}.4827$	—
	1.798	0.8045	26.3	0.03502	$\bar{2}.5444$	5.589
5.734	0.000	0.8042	—	0.00375	$\bar{3}.5740$	—
	1.061	0.8150	24.3	0.01061	$\bar{2}.0257$	0.428
9.649	0.000	0.8200	—	0.004200	$\bar{3}.6514$	—
	0.9131	0.8290	24.0	0.01552	$\bar{2}.1942$	0.594

TABLE VIII

Viscosity of nitro cotton sols in dry methyl ethyl ketone and in methyl ethyl ketone-water mixtures

(Sols shaken for 22 hours at 55.0° in dark, measured at 25.00°C)

Concn. water %	Concn. N.C. %	$d^{55°}_{4°}$ of sol gms./cc.	Age hours	η poises	log η	slope $\frac{\log \eta/\eta_0}{\text{concn.}}$
0.00	0.000	0.8013	—	0.004976	$\bar{3}.6969$	—
	0.8303	0.8096	25.3	0.01368	$\bar{2}.1361$	0.529
6.904	0.000	0.8168	—	0.00558	$\bar{3}.7466$	—
	0.8555	0.8254	25.1	0.01073	$\bar{2}.0306$	0.332
28.36	0.000	0.8660	—	0.006332	$\bar{2}.8015$	—
	0.9802	0.8758	27.5	0.03866	$\bar{2}.5872$	0.802

---

[1] J. Soc. Chem. Ind., **42**, 207-211T (1923).

Harvey and Squance found for slopes in formanilide 1.08, in form-ortho-toluidide 0.1-0.2 and in a 50% mixture of the two 0.78. Hence, the absolute viscosity of the mixture (0.614) is distinctly less than the mean for the two solvents (1.086 and 0.4 or 0.5, mean 0.75 or 0.8).

The addition of six parts of the non-solvent benzene, to one of acetone greatly raises the viscosity slope though it is still equal to that of ethyl phenyl urethane or methyl phenyl urethane.

Smith investigated four mixtures of non-volatile solvents in equal parts by weight at 55° under standard conditions. The results are given in Table IX.

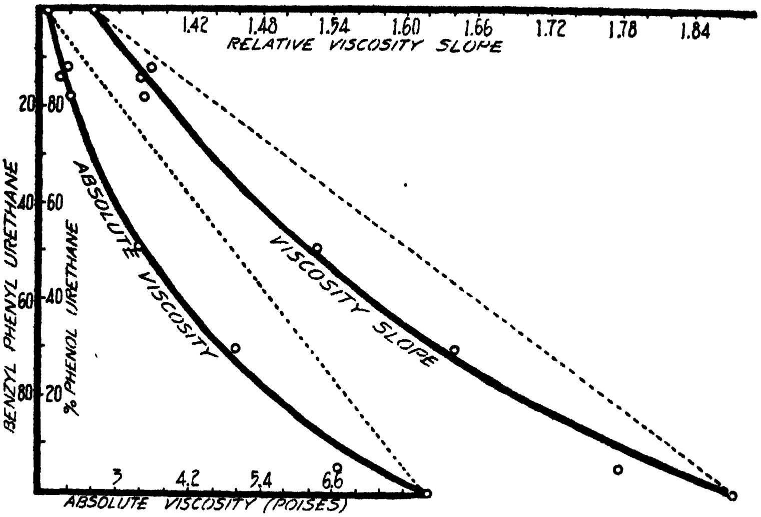


FIG. 3

Viscosities and slopes of relative viscosities of solutions of nitro cotton in phenyl methane and ortho tolyl methane and their mixtures.

TABLE IX

Absolute viscosities and viscosity slopes $\frac{(\log \eta/\eta_0)}{\text{concn.}}$ of solutions in mixed solvents compared with the values in the pure solvents separately

	Viscosity slope				Absolute viscosity, η (poises)			
1st pure solvent	BPU*	B formanil.	EtPhth.	PU	BPU	B formanil.	EtPhth.	PU
	2.108	1.174	2.118	1.673	14.10	1.720	5.606	4.05
2nd pure solvent	EtPhth.	MeCyanil	Benz.	oTU	Etphth.	MeCyanil.	Benz.	oTU
	2.118	1.189	1.882	2.116	5.606	0.3148	3.534	9.616
Mean	2.113	1.186	2.00	1.895	9.853	1.0174	4.570	6.835
Mixture	2.12	1.10	1.72	1.38	8.349	0.4987	2.258	1.963
% decrease	0%	7%	14%	27%	15%	51%	51%	71%

(* Phenyl urethane = PU; ortho-tolyl urethane = oTU; ethyl phthalate = EtPhth.; benzyl phenyl urethane = BPU; benzyl formanilide = B formanil.; methyl cyanilide = MeCyanil.; Benzophenone = Benz.)

Miss M. E. Grant has carried out a series of determinations with mixtures of phenyl urethane and benzyl phenyl urethane in all proportions at 55° under standard conditions. The results are shown graphically in Fig. 3. Both viscosity slope and absolute viscosity of the solutions are plotted (continuous curves) and each is compared with the values found by linear interpolation of the values found for nitro cotton in the two solvents separately. In the case of the viscosity slope this may or may not be legitimate because the observed slopes are necessarily referred to the observed viscosity of the mixed solvents themselves which passes through a maximum value, whereas no such maximum can be taken in predicting the mixed slopes. However, it is seen that the observed slopes are smaller than the slopes expected from the behavior of solutions in the separate solvents.

It will be seen that the absolute viscosities like the slope do not pass through a minimum value, because the viscosities in the separate solvents lie too far apart. However, the observed values for the actual viscosities are unmistakably lower than those obtained by linear interpolation from solutions in the separate solvents. In other words, although there is no optimum solvent the behavior of the mixture is better than would be expected from the behavior of the separate components. Thus, the poorer solvent is less detrimental to solvent power than expected and the better solvent is more beneficial than expected.

Apart from the mixtures which definitely give an optimum solvent, forming solutions of nitro cotton whose viscosity no matter how calculated or compared is less than that of corresponding substances or solutions in either single constituent, it is probable that in all cases the absolute viscosity of the solution in the mixture is definitely lower than that predicted from solutions in the two pure solvents. Absence of a minimum is in some cases due to the fact that the viscosities of the solutions in the separate solvents lie too far apart.

The evidence is overwhelming that in almost all cases a mixture of solvents in suitable proportions has greater solvent power than that of the mean of the two solvents. Our suggested explanation lies in the direction of assuming that certain molecular grouping in each substance have a specific power of combining with definite groupings in the nitro cellulose complex differing from substance to substance. Table X summarises all known cases, including those we have ourselves investigated, where the solvent power for nitro cotton of a mixture surpasses that of any single constituent of the mixture.

TABLE X

The behavior of all known mixtures of solvents for nitro cotton

1. *Optimum solvent from 2 non-solvents.*
    Ether-alcohol.
    Camphor-alcohol.

(Table X continued on page 328)

2. *Optimum mixtures from 2 solvents.*
    - Methyl alcohol-acetone.
    - Acetic acid-acetone.
    - Acetic acid-ether: alcohol.
    - Ethyl phthalate-benzophenone.
    - Phenyl urethane-o-tolyl urethane.
    - Benzyl formanilide-methyl cyanilide.
3. *Improved solvent by adding a non-solvent to solvent.*
    - Toluene-alcohol (for a low nitrogen nitro cotton--Sproxton)
    - Benzene-alcohol (aq.)
    - Water-acetone.
    - Water-methyl ethyl ketone.
    - Water-alcohol at low temperatures (I. Masson)
    - Water-ether: alcohol.
    - Amyl acetate-ether: alcohol.
    - Alcohol-camphor.
    - Alcohol-acetophenone.
    - Alcohol-benzyl ethyl ether.
    - Alcohol-benzyl phenyl urethane.
    - Alcohol-acetone.
    - Alcohol-diethyl carbonate.
    - Butyl alcohol-butyl acetate.
4. *The only mixtures which are not known to give an optimum solvent.*
    - Benzene-acetone.
    - Toluene-acetone.
    - (Formanilide-form-o-toluidide)
    - (Benzyl phenyl urethane-ethyl phthalate)
    - Benzyl phenyl urethane-phenyl urethane.

It is interesting to quote from the summary of Mardles' paper[1] on "Solvent Power of Mixtures for Cellulose Acetate and Nitrate":—

"The close correlation of the solvent power of a liquid or mixture of liquids for a cellulose ester, and the viscosity of the solution is, apart from the theoretical interest, of considerable industrial importance. It involves the economy of costly solvents and time in preparation of the cellulose ester varnishes. The optimum solvent mixture dissolves the cellulose ester most rapidly; because the least viscous solutions are formed and the particles diffuse most rapidly away from the dissolving material. The solutions so prepared are also the clearest, the degree of dispersion being usually highest. They are generally the most stable since the tendency to set to a jelly is at a minimum[2]

"That the optimum solvent mixture should possess the maximum fluidity, follows from the fact that with the highest degree of dispersion, there is the nearest approach to a true (molecularly dispersed) solution with its characteristically low viscosity."

---

[1] J. Soc. Chem. Ind., **42**, 211T (1923).

[2] Cf. E. Mardles: Trans. Faraday Soc., **18**, Part 3 (1923).

9. *The viscosity of the solutions of one definite sample of nitro cotton in various solvents under definite conditions at 55° is inversely proportional to their solvent power.*

(*a*) *The data*

Considerations of space forbid publication of our long series of measurements on many hundred independent solutions many of which were kept for long periods and repeatedly studied. Each recorded result was the mean of three determinations and solutions were almost always made up in duplicate so that final values were usually the mean of six determinations. To illustrate the results Table XI is here taken from L. E. Smith's Series II.

The results are all finally expressed in the form of mean slope; that is, the log of the ratio of the viscosity of the solution to the viscosity of the solvent divided by the concentration, it being assumed (merely as a basis for numerical comparison) that this slope has a constant value for solutions up to 0.5% of nitro cotton. Where a series of dilutions were made the slope is usually the mean of three dilutions of two independent duplicate solutions but in Smith's later work it was considered sufficient if good agreement were obtained with two independent duplicate solutions. The age of the solution was taken from the first mixing of nitro cotton and solvent and the duration of the initial standard shaking was 22 hours. Our standard procedure was developed by C. E. Harvey, the final details being fixed by H. B. Bennett and L. E. Smith.

TABLE XI

Smith Series II. Solutions prepared and measured at 55° in the dark. Standard shaking

N.C. %	$D^{55°}_{4°}$	Age	Tube	Viscosity (poises)	log η	slope $\frac{(\log \eta/\eta_0)}{\text{concn.}}$
Benzyl phenyl urethane.						
0.395	1.080	24.0 hrs.	N	0.6679	$\bar{1}.8247$	1.98
0.3374	1.0793	24.0	N	0.5248	$\bar{1}.7200$	2.01
Pure	1.076		2AG	0.1098	$\bar{1}.0407$	*Mean* = *1.995*
0.395	1.080	14 days	N	0.3685	$\bar{1}.6664$	1.33
0.3374	1.0793	14	N	0.3020	$\bar{1}.4800$	1.30
						Mean = *1.315*
0.395		84	P	0.1932	$\bar{1}.2860$	0.620
0.3374		84	P	0.1718	$\bar{1}.2848$	0.577
						Mean = *0.599*
0.395		175	P	0.1602	$\bar{1}.2047$	0.405
0.3374		174	P	0.1433	$\bar{1}.1562$	0.343
						Mean = *0.375*

(Table XI continued on page 330)

TABLE XI (continued)

N.C. %	$D^{55°}_{4°}$	Age	Tube	Viscosity (poises)	Log η	Slope $\left(\frac{\log \eta/\eta_0}{\text{concn.}}\right)$
		Ethyl phthalate (Nobel's Dec. 1923)				
0.3522	1.0905	24.3 hrs.	N	0.2202	$\bar{1}.3428$	2.04
0.355	1.0905	24.0	P	0.2266	$\bar{1}.3353$	2.05
Pure	1.087		1AG	0.4215	$\bar{2}.6248$	*Mean = 2.045*
0.3522	1.0905	14 days	N	0.2076	$\bar{1}.3173$	1.97
0.355	1.0905	14	P	0.215	$\bar{1}.3325$	1.99
						Mean = 1.98
0.3522		84	P	0.1526	$\bar{1}.1835$	1.58
0.355		84	P	0.1485	$\bar{1}.1718$	1.54
						Mean = 1.56
0.3522		174	P	0.1177	$\bar{1}.0708$	1.27
0.355		170	P	0.1173	$\bar{1}.0693$	1.25
						Mean = 1.26
		Ethyl phthalate (Kodak)				
0.4049	1.091	24.0 hrs.	P	0.266	$\bar{1}.4248$	1.98
0.420	1.091	23.9	P	0.2807	$\bar{1}.4483$	1.96
Pure	1.087		1AG	0.041	$\bar{2}.6243$	*Mean = 1.97*
0.4049	1.091	14 days	P	0.2214	$\bar{1}.3453$	1.78
0.420	1.091	14				
0.4049		84	1AG	0.06763	$\bar{2}.8301$	0.534 = *0.534*
0.4049		168	1AG	0.05894	$\bar{2}.7704$	0.362 = *0.362*
		Ethyl formanilide (May 1924)				
0.4076	1.028	24.0 hrs.	1AG	0.05495	$\bar{2}.7400$	0.875
0.4729	1.0287	24.0	1AG	0.06204	$\bar{2}.7937$	0.87
Pure	1.024		1AG	0.02418	$\bar{2}.3834$	*Mean = 0.872*
0.4076	1.028	14 days	1AG	0.03673	$\bar{2}.5651$	0.446
0.4729	1.0287	14	1AG	0.04118	$\bar{2}.6146$	0.489
						Mean = 0.467
0.4076		84	1AG	0.02896	$\bar{2}.4618$	0.193
0.4729		84	1AG	0.03045	$\bar{2}.4836$	0.214
						Mean = 0.203
0.4076		170	1AG	0.02743	$\bar{2}.4383$	0.111
0.4729		169	1AG	0.02828	$\bar{2}.4514$	0.144
						Mean = 0.127
		Ethyl phenyl urethane (March 1923)				
0.3743	1.017	24.0 hrs.	P	0.1327	$\bar{1}.1230$	1.82
0.4026	1.017	23.8	1AG	0.1446	$\bar{1}.1603$	1.78
Pure	1.013		1AG	0.02760	$\bar{2}.4409$	*Mean = 1.80*
0.3743	1.017	15 days	1AG	0.08408	$\bar{2}.9247$	1.29
0.4026	1.017	14	1AG	0.0936	$\bar{2}.9713$	1.32
						Mean = 1.31

TABLE XI (continued)

N.C. %	$D^{55°}_{4°}$	Age	Tube	Viscosity (poises)	log η	Slope $\left(\frac{\log \eta/\eta_0}{\text{concn.}}\right)$
Ethyl phenyl urethane (March 1923) (cont'd.)						
0.4076		84 days	1AG	0.04246	$\bar{2}.6280$	0.50
0.4026		84	1AG	0.05802	$\bar{2}.7636$	0.803
						Mean = 0.651
0.3743		168	1AG	0.03795	$\bar{2}.5791$	0.369
0.4026		169	1AG	0.04288	$\bar{2}.6322$	0.476
						Mean = 0.422
Methyl phenyl urethane (8/8/23)						
0.403	1.045	24.0 hrs.	N	0.1131	$\bar{1}.0535$	1.6
0.3539	1.0455	24.1	1AG	0.09562	$\bar{2}.9806$	1.61
Pure	1.042		1AG	0.02569	$\bar{2}.4079$	*Mean = 1.605*
0.403	1.046	14 days	1AG	0.07252	$\bar{2}.8605$	1.12
0.3539	1.0455	14	1AG	0.0675	$\bar{2}.8293$	1.18
						Mean = 1.15
0.403		84	1AG	0.4702	$\bar{2}$ 6723	0.652
0.3539		84	1AG	0.4158	$\bar{2}.6188$	0.591
						Mean = 0.621
0.403		168	1AG	0.03702	$\bar{2}.2984$	0.395
90.353		168	1AG	0.03413	$\bar{2}.5332$	0.349
						Mean = 0.372
Formanilide (Nobel's)						
0.3498	1.1175	24.9 hrs.	P	0.1987	$\bar{1}.2984$	1.01
0.3341	1.117	24.2	P	0.1944	$\bar{1}.2888$	1.03
Pure	1.114		1AG	0.08794	$\bar{2}.9442$	*Mean = 1.02*
0.3498	1.1175	14 days	1AG	0.1302	$\bar{1}.1145$	0.487
0.3341	1.117	14	1AG	0.1260	$\bar{1}.1003$	0.468
						Mean = 0 477
0.3498		84	1AG	0.1013	$\bar{1}.0058$	0.175
0.3341		84	1AG	0.09886	$\bar{2}.9981$	0.152
						Mean = 0.163
0.3498		169	1AG	0.09324	$\bar{2}.9696$	0.073
0.3341		168	1AG	0.09269	$\bar{2}.9670$	0.068
						Mean = 0.070

TABLE XI (continued)

N.C. %	$D^{55°}_{4°}$	Age	Tube	Viscosity (poises)	$\log v$	Slope $\frac{\log v/v_0}{\text{concn.}}$
o-Tolyl urethane (15/4/24)						
0.371	1.089	24.1 hrs.	P	0.3175	$\bar{1}.5018$	1.7
0.3963	1.065	24.1	P	0.3583	$\bar{1}.5542$	1.73
Pure	1.061		1AG	0.07425	$\bar{1}.8707$	*Mean = 1.715*
0.371	1.0647	14 days	P	0.2328	$\bar{1}.3670$	1.34
0.3963	1.065	14	P	0.2617	$\bar{1}.478$	1.38
						Mean = 1.36
0.371		84	P	0.1319	$\bar{1}.1202$	0.672
0.3963		84	P	0.1351	$\bar{1}.1306$	0.665
						Mean = 0.669
0.371		168	1AG	0.1033	$\bar{1}.0010$	0.352
0.3963		168	1AG	0.1049	$\bar{1}.0208$	0.379
						Mean = 0.365
Phenyl urethane (Aug. 1923)						
0.405	1.088	23.9 hrs.	P	0.3223	$\bar{1}.5083$	1.42
0.4093	1.089	24.2	P	0.3337	$\bar{1}.5233$	1.45
Pure	1.085		1AG	0.08535	$\bar{2}.9313$	*Mean = 1.435*
0.405	1.089	14 days	P	0.1745	$\bar{1}.2417$	0.765
0.4093	1.089	14	P	0.1799	$\bar{1}.2551$	0.792
						Mean = 0.778
0.405		84	1AG	0.111	$\bar{1}.0457$	0.283
0.4093		84	1AG	0.1102	$\bar{1}.0422$	0.272
						Mean = 0.277
0.405		168	1AG	0.09927	$\bar{2}.9968$	0.163
0.4093		168	1AG	0.09865	$\bar{2}.9941$	0.153
						Mean = 0.158
Benzophenone (Nov. 1923)						
0.3506	1.0845	24.2 hrs.	P	0.166	$\bar{1}.2200$	1.59
0.351	1.0845	24.0	P	0.165	$\bar{1}.2173$	1.57
Pure	1.081		1AG	0.04601	$\bar{2}.6629$	*Mean = 1.58*
0.3508	1.0845	14 days	1AG	0.111	$\bar{1}.0451$	1.09
0.307	1.0845	14	1AG	0.1132	$\bar{1}.0542$	1.11
						Mean = 1.10
0.3508		84	1AG	0.06336	$\bar{2}.8018$	0.396
0.351		84	1AG	0.06503	$\bar{2}.8131$	0.428
						Mean = 0.412
0.3508		168	1AG	0.05697	$\bar{2}.7556$	0.264
0.351		168	1AG	0.05902	$\bar{2}.7711$	0.309
						Mean = 0.286

TABLE XI (continued)

N.C. %	$D^{55^\circ}_{4^\circ}$	Age	Tube	Viscosity (poises)	log η	Slope $\left(\frac{\log \eta/\eta_0}{\text{concn.}}\right.$
		Benzyl formanilide (1/10/20)				
0.4032	1.104	24.2 hrs.	P	0.3773	$\bar{1}.5767$	1.29
0.3512	1.1035	24.0	P	0.3323	$\bar{1}.5215$	1.30
Pure	1.100		1AG	0.1160	$\bar{1}.0647$	*Mean* = *1.295*
0.4032	1.104	14 days	P	0.2169	$\bar{1}.3363$	0.67
0.3512	1.1035	14	P	0.2065	$\bar{1}.3150$	0.71
						Mean = *0.69*
0.4032		84	P	0.1760	$\bar{1}.2455$	0.488
0.3512		84	P	0.1784	$\bar{1}.2263$	0.460
						Mean = *0.454*
0.4032		168	P	0.1699	$\bar{1}.2302$	0.410
0.3512		168	P	0.1675	$\bar{1}.2241$	0.460
						Mean = *0.432*
		Benzyl formanilide (16/2/25)				
0.3632	1.1036	24.0	P	0.3426	$\bar{1}.5347$	1.29
0.4723	1.1047	24.2	P	0.4171	$\bar{1}.6202$	1.17
Pure	1.100		1AG	0.1163	$\bar{1}.656$	*Mean* = *1.23*
0.3643	1.100	14 days		0.2065	$\bar{1}$ 3150	0.687
0.4723		14	P	0.2616	$\bar{1}.4175$	0.744
						Mean = *0.73*
		Benzophenone (Kahlbaum)				
0.3554	1.0845	24.2 hrs.	1AG	0.2493	$\bar{1}.3967$	2.04
Pure	1.081		1AG	0.03688	$\bar{2}.6709$	*Mean* = *2.04*
		Benzophenone (Nobel's 2/4/25)				
0.3952	1.085	24.2 hrs.	P	0.2305	$\bar{1}.3636$	1.76
Pure	1.081		1AG	0.04647	$\bar{2}.6672$	*Mean* = *1.76*

(*b*) *Discussion of results.*

In the previous section attention was drawn to the fact that the final viscosity of the solutions and hence the viscosity slope was greatly influenced by the purity of the solvent. In general the solvents used latterly have been purer than those used formerly.[1] It has been pointed out that within certain limits the less impure the solvent the lower the slope. The slopes have been systematically raised during later work owing to the increased purity of the solvents.

---

[1] All were obviously much purer than ordinary commercial solvents.

Considering the solvents as a whole, the slopes vary from about 0.5 to about 2.2, the slopes in the poorest solvents being over four times as great as those in the best solvents. The slopes of the substituted urethanes are of the same order of magnitude, also those of formanilide and the substituted formanilides are of the same order. The similarity of the slopes of similar substances will be further brought out when considering the ageing of these solutions. The substances which do not belong to any definite group are scattered between the extremes of the good and bad "gelatinizers."

It has been assumed that the best time for comparing the viscosities of the nitro cotton solutions is at 24 hours after the mixing of the nitro cotton and solvent. Under the fixed conditions of shaking that are in use, the time taken for the complete solution of the gel in the solvent varies considerably. The time for solution may be taken as being roughly proportional to the slope for the particular solvent (for a given concentration) and not, as might be expected, to the absolute viscosity, 24 hours is a convenient time to take the initial measurement of the viscosity, because all solutions are complete within that time. Formanilide, which is a fairly viscous liquid dissolved 0.5% of nitro cotton in about 2 hours, whereas ethyl phthalate and others which are less viscous require several hours more shaking. If it be considered that 24 hours is not the best time for making the comparison, then this can be done at a greater age; this will be dealt with under the ageing of nitro cotton in a later section (II).

The justification for comparing the viscosity effects for the various solvents through the medium of viscosity slope is given in the following theoretical paper. The whole of the existing data for slopes at 55° at age 24 hours is compiled in Fig. 4. In this graph the various solvents are put in parallel columns in a somewhat arbitrary order but keeping the urethanes and the anilides together. An ordinates the viscosity slopes are employed and the viscosity slope found by each worker is indicated at the appropriate height by a short horizontal line. Furthermore, the results are weighted by the use of lines of various thicknesses and forms to distinguish the most accurate work done under standard conditions. Finally, just above each line is given the letter referring to the specimen of solvent actually used, the specimens having been arranged in chronological order; the earliest, generally the least pure, being given the letter A, Kahlbaum's chemicals being marked K.

Inspection of the graph brings out very clearly the relations between the solvents in spite of all subordinate influences such as degree of possible impurity. First and most important is that the different solvents definitely give different viscosity slopes with the same specimen of nitro cotton. This disproves J. Duclaux and Mme. Wollman's suggestion[1] that the slope is independent of the solvent and it is more conclusive in that the specimen of nitro cotton we have employed throughout is particularly homogeneous, all coming down in one fraction under the conditions of Duclaux' experiments on fractionation.

---

[1] Bull., 22, 414 (1920).

The second generalisation is that molecular weight is an important factor in a series of closely similar compounds. The lower the substance in the homologous series the better the solvent. This rule does not rest upon a very wide basis but it is illustrated within the group of five urethane and with the three formanilides, and in a comparison of acetophenone with benzophenone.

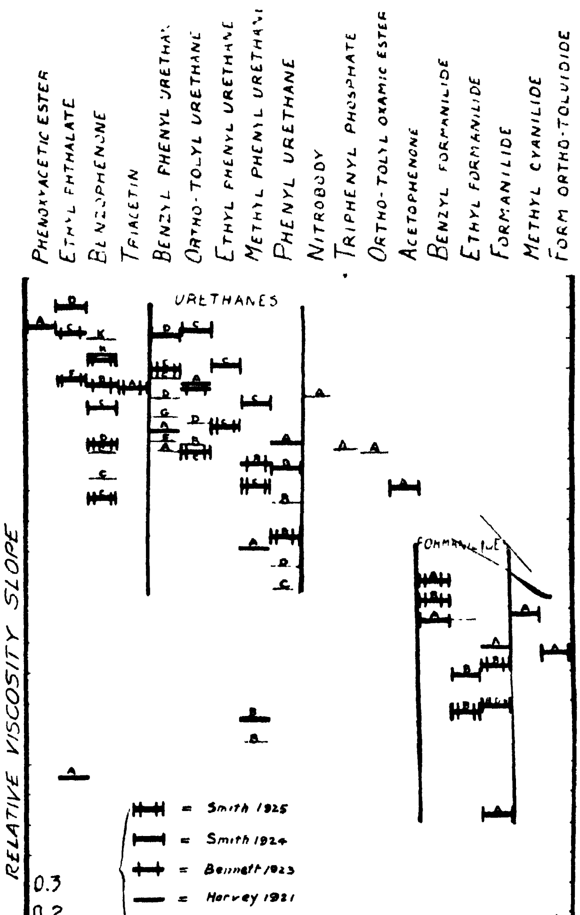


Fig. 4

Relative viscosity for unit concentration of one specimen of nitro cotton dissolved in different samples of various solvents at 55° under highly comparable conditions.

Mardles[1] has observed that the same rule holds for solutions of cellulose acetate.

It is taken for granted in this discussion that the best solvents are those which give the lowest viscosity slopes in accordance with the suggestion put forward by Schwartz[1] and adopted by most of the succeeding workers on this subject.

---

[1] J. Soc. Chem. Ind., **42**, 128T (1923).

The theoretical interpretation of this result is given in the following theoretical paper. The longer we have worked the more we have been impressed with the close relation between low viscosity slope and solvent power as deduced from other indications. For example, solutions with lowest viscosity slopes are found with the solvents in which the nitro cotton most quickly dissolves and in which the highest concentrations can be prepared.

A third point is that the formanilides are all much better than the urethanes and esters are fairly comparable with urethanes. Keyes[2] has pointed out that the reason why commercial esters are so much better solvents than pure esters is that they generally contain free alcohol.

It is worth while reproducing a table showing our earlier results with the impure solvents as ordinarily used and giving the comparison with these same materials and their reputation in factory tests. The fact that in certain cases there were wide divergences in the factory reputation of these materials as tested on various occasions is readily explained in the light of our later work which has brought out so clearly the connection between suitable admixture of solvents and solvent power.

TABLE XII

Relative slopes of viscosity-concentration curves compared with solvent power at 55°C. (Measurements by Harvey, Miss King and W. A. Squance with less pure materials)

Solvent	Mean slope	Reputed solvent power
Form-o-toluidide	(0.1567)	Good
Ethyl phthalate	0.6596	Very good
Formanilide: form-o-toluidide Mixture	0.7765	Very good
Ethyl phenyl urethane	0.8327	Very good
Formanilide	1.084	Very good
Ethyl formanilide	1.316	Very good
Methyl phenyl urethane	1.384	Very good
o-Tolyl oxamic ester	1.387	Fair
Triphenyl phosphate	1.727	——
Benzyl phenyl urethane	1.757	Fair
o-Tolyl urethane	1.782	Fair
Nitrobody	1.897	——
Phenyl urethane	1.960	Poor
Benzophenone	2.06	Poor

---

[1] Kolloid-Z., **12**, 32-41; J. Soc. Chem. Ind., **32**, 191 (1913).

[2] J. Ind. Eng. Chem., **17**, 563 (1925).

(c) *Conclusion.*

The viscosity of solutions of nitro cotton even when calculated according to the Arrhenius formula which relates it to those of the solvents depends greatly upon the nature of the solvent, contrary to the suggestion of Duclaux and Wollman.

Low relative viscosity may be taken as a general measure of solvent power.

Increase of molecular weight with comparable compounds impairs solvent power and increases relative viscosity.

The formanilides are a much better group of solvents than the urethanes or the pure esters.

10. *Nitro cotton is only very slightly decomposed on heating in solution for long periods at very moderate temperatures.*

In every solvent we have studied at 55° or higher temperatures the viscosity of the solution of nitro cotton diminishes with time. The higher the temperature the more rapid as well as extensive is the diminution so that even a brief exposure to a high temperature such as 90° permanently diminishes the viscosity. If one portion of a solution is kept at 55° and another portion heated for a short time to 90° or if it is prepared at 90° and then kept at 55° the viscosity of the second portion is much lower than that of the first portion even after the lapse of months.

We are of the opinion that the effects we have observed are essentially due to "degradation" of the nitro cotton and not to its denitration or to nitration of the solvent at its expense. To disprove the last two alternatives several tests have been carried out from time to time.

Reid found that nitro cotton recovered from aged solutions yielded new solutions which although somewhat less viscous still aged at 55°. Squance recovered methyl phenyl urethane which had had 20% nitro cotton dissolved in it for a fortnight and tested for nitration with a negative result. Furthermore, all the solutions, including such solvents as ethyl phthalate and benzophenone behave similarly as regards ageing although many of them do not nitrate at all under ordinary conditions. Lastly, Baker's work on alcoholic solutions as well as that of Tainsh (not published) seemed to show it was a mere "physical degradation" of the nitro cotton.

(b) *Analysis for NO_2 group by Bennett.*

The most careful tests were those reported by H. B. Bennett in 1922 and 1923. To save space all details of standardization, procedure and analyses are here omitted. Three highly concentrated solutions (C, D and E) were prepared in methyl phenyl urethane at 90° and kept for a week or two at that temperature and the recovered solvents quantitatively analyzed for nitro groups by reduction with titanous sulphate. One solution (F) was kept for 4½ months at 90° in a sealed tube and when opened after this very drastic treatment it was found to be distinctly under pressure (presumably N_2—possibly some NO). The analytical results for this solution is given in detail.

Results of nitration analysis.

The time of extraction for each of the analyses below was approximately 24 hours, but the degree of extraction for solution D (24.43%) was not so high as for solution E and solution C. The extent of the nitration of the solvent was estimated as the per cent weight of available nitro cotton used up in nitrating the solvent, taking the total nitro cotton present as 100% (the sample of nitro cotton used contained 12.11% nitrogen by weight).

TABLE XIII

Soln.	N.C. %	Age of soln.	Wt. in gms. of soln. taken.	Vol. $Ti_2(SO_4)_3$ soln. added (ccs)	Vol. from alum soln. added.	Vol. $Ti_2(SO_4)_3$ soln. used up. (ccs)	Proportion of N.C. used up in nitration.
C	30	6 days	8.75	99.54	90.52	3.51	0.38%
D	25	8	10.21	49.72	45.07	1.90	0.24
E	20	14	12.11	64.69	56.53	4.73	0.71

Hence, in the three cases the nitro cotton which originally contained 12.10% nitrogen now contains at least 12.06%, 12.08% and 12.03% nitrogen respectively still in spite of two days at 90° and a subsequent 1 or 2 weeks at room temperature.

Solution F was prepared by shaking at 90° in a sealed tube for 3 days and stored for over 4½ months (141 days) at approximately 90°. The result was as follows.

TABLE XIV

Soln.	% concn. of N.C. soln.	Wt. of N.C. soln. taken for extraction.	Vol. of $Ti_2(SO_4)_3$ solution added	Vol. iron alum solution added	Vol. $Ti_2(SO_4)_3$ solution used up.	Proportion of N.C. used up in nitration.
F	19.92	17.06	129.20	47.39	47.92	1.55%

Therefore the nitro cotton which was 12.10% is not still at least 12.10 − 0.154 = 11.95% nitrogen.

(*c*) *Discussion.*

The view that the nitration of any of the solvents by nitro cotton is not appreciable has been substantiated by direct test of the extent of nitration of methyl phenyl urethane under the very drastic conditions of keeping concentrated solutions at 90° for periods of one week to 4½ months. In the shorter periods much less than 1% of the available nitro groups in the nitro cotton and in the most prolonged experiments only 1.55% of the available nitro groups in the nitro cotton had combined with the solvent.

Hence, the conclusion is confidently drawn that the large amount of ageing which takes place during the first few hours and days at the very much lower temperature of 55° in all solvents alike cannot be due to denitration of the nitro cotton by the solvent.

In the experiments described in section 3 one factor was isolated; namely, the degradation of the nitro cotton itself apart from any possible interaction with solvent on heating it alone at 60°. Here the total fall of slope in a fortnight was not more than about 12% whereas in ordinary ageing experiments at the distinctly lower temperature of 55° the decrease in slope in the same period is 50% or four times greater. This is in spite of the fact that the heating of the nitro cotton alone at 60° includes both any spontaneous denitration and physical degradation of the nitro cotton itself.

(*d*) *Conclusion.*

It is concluded that in quite typical cases of ageing of solutions at 55° any possible effect of denitration of nitro cotton by interaction with the solvent must be inappreciable even after very long periods. The ageing effect of heating nitro cotton by itself at 60° which is in accordance with our general working hypothesis that the chief factor in the diminution of apparent viscosity is due to the disintegration of the colloidal aggregates into smaller particles through interaction with the solvent.

11. *The viscosity of solutions of nitro cotton kept at 55° for very long periods diminishes approximately proportional to the logarithm of the time.**

(*a*) *Summary of previous knowledge.*

Invariably, the viscosity of a solution of nitro cotton in any solvent we have used diminishes on keeping the solution at 55° and 90°. In view of the previous section this cannot be ascribed to denitration of the nitro cotton.

An approximate idea of the magnitude of ageing may be gathered from the statement that the viscosity slopes observed at one day old are reduced to about one half in three weeks and to about a quarter in three months.

Doubtless solutions or temperatures could be found where the apparent viscosity would increase with time and the solution might even set to a jelly.[1] We have probably missed this by working at so high a temperature as 55°.

The ageing or decrease in viscosity is continuous being rapid at first and apparently not reaching a limiting value even after months or perhaps years. The decrease in viscosity is greater at 90° than at 55°. Early solutions which were kept at room temperature changed to a much less extent.

Masson and McCall[2] studied nitro cotton in aqueous acetone and ether-alcohol solutions. With acetone and aqueous acetone the viscosity almost immediately assumed a maximum value from which it fell very gradually; no numerical data are given. As far as it goes this behavior agrees with that observed here.

---

[1] Only in one solvent, benzyl formanilide, was this diminution in viscosity interrupted. After many months at 55° during which time the viscosity fell off, such solutions set to a soft jelly. If they were then resubmitted to standard shaking for one or two days at 55° they were liquefied; but the viscosity was distinctly above the expected place on the ageing curve and they quickly set again to a jelly, the viscosity rising rapidly even during the actual measurement. The jelly did not melt upon merely raising the temperature to 90°.

[2] J. Chem. Soc., **117**, 819 (1920).

Ether-alcohol behaved similarly in the case of the mixture of ether and alcohol in which nitro cellulose has least viscosity. If however the relative proportions of ether and alcohol differ widely from the optimum ratio the viscosity is not fully developed, even after 100 hours,—this in spite of very vigorous agitation followed by mechanical shaking. It would be interesting to inquire whether the sols had been completely formed in these cases.

Masson and McCall concluded that two processes occur, first the adsorption of solvent by nitro cellulose which is accompanied by the solvation of the resulting gel, and secondly a change in the dispersed gel *not* necessarily accompanied by any alteration in the percentage composition of the particles, but probably to be ascribed to a change in their state of aggregation. The former process is very rapid with acetone and optimum ether-alcohol, although with other ether-alcohol mixtures the adsorption of solvent is slow. In all cases the complete disintegration of the particles or their aggregates is very slow. As we point out elsewhere, we should explain disaggregation as being

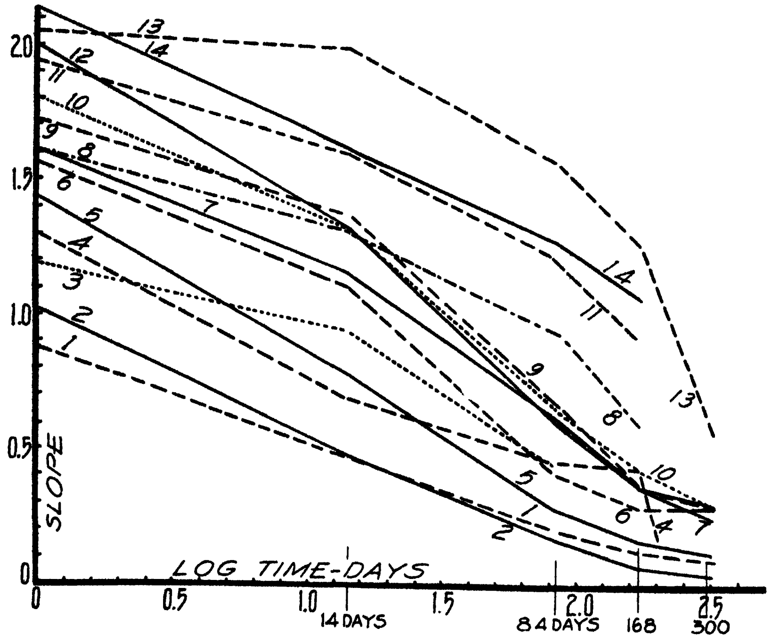


FIG. 5

Change in slope of relative viscosity of solutions of nitro cotton in various solvents measured at intervals up to a year.

Key

1. Ethyl formanilide
2. Formanilide
3. Methyl cyanilide
4. Benzyl formanilide
5. Phenyl urethane
6. Benzophenone
7. Methyl phenyl urethane
8. Acetophenone
9. Ortho tolyl urethane
10. Ethyl phenyl urethane
11. Triacetin
12. Benzyl phenyl urethane
13. Ethyl phthalate
14. Phenoxyacetic ester.

caused by solvation. Incidentally it may be mentioned that none of the preposed formulae of the viscosity concentration curve were strictly applicable. Leyseiffer[1] studied nitro cellulose (from wood) in acetone at 20°C., and found that the viscosity in acetone fell off slightly during a month, following the first measurements at the age of 15 hours. This decrease was greatest for the most viscous solutions. Schwartz had found in 1913 that viscosity in camphor-alcohol doubles in a fortnight after the first half hour, but, like Peist in 1910, who usually observed but little change, he was unable to get reproducible results, and sometimes observed a decrease and sometimes an increase.

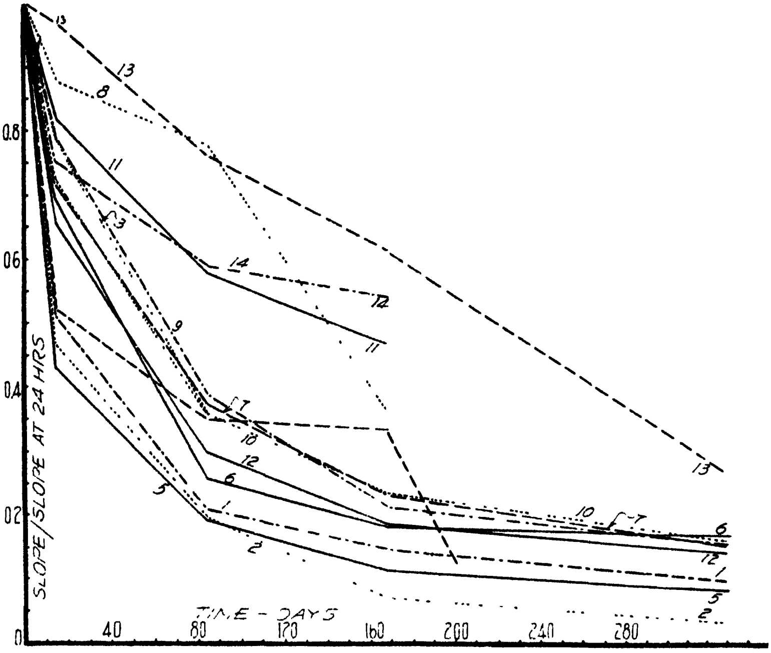


FIG. 6

Change with time in relative viscosity slope of solutions of nitro cotton taking the value at 24 hours in each case as unity.

Key

1. Ethyl formanilide
2. Formanilide
3. Methyl cyanilide
4. Benzyl formanilide
5. Phenyl urethane
6. Benzophenone
7. Methyl phenyl urethane
8. Acetophenone
9. Ortho tolyl urethane
10. Ethyl phenyl urethane
11. Triacetin
12. Benzyl phenyl urethane
13. Ethyl phthalate
14. Phenoxyacetic ester.

It is important in view of the above to note that most workers have ignored the possibility of ageing effects and that their work must be in many cases appreciably modified thereby.

(*b*) *Data up to long periods* (*one year*).

Here again most of our data are suppressed for lack of space, although series of experiments have been carried out by six of us. Typical data using the latest technique may be found in the previous Table XI where the tubes were sealed and maintained at 55° in the dark.

---

[1] Kolloidchem. Beihefte, 10, 145-178 (1918).

Wholly independent duplicate determinations at age 24 hours usually agree in viscosity to within about 1% but large divergences develop after storage.

When slope is plotted against log of time for solutions of nitro cotton in a large number (14) of solvents as in Fig. 5, the general effect is a number of parallel straight lines. That is, the slopes diminish in absolute value in proportion to the log of the age of the solution and all at about the same absolute rate. The solutions showing originally the least viscosity would take about a year to approximate to the viscosity of a crystalloidal solution or to that of the solvent itself, whereas the worst solvents with the highest slopes would require about 60 years to do the same.

If all the slopes are divided by the slope for the same solution at the age of 24 hours; in other words if the initial slope is taken as unity for each solution and these relative slopes are plotted against times as in Fig. 6 it is found on examining the curves that the best solvents are those which relatively age most in a given time. Broadly speaking, the graphs maintain their relative

TABLE XV

Ageing of solutions of nitro cotton at 25°

Solvent	Concn.	Age	Viscosity (poises)	Slope
Benzyl phenyl urethane (25/12/22)	0.5288	1 day	1.167	1.934
		12 weeks	1.042	1.841
	0.5500	1 day	1.480	2.047
		6 weeks	1.404	2.005
	0.5288	1 day	1.267	2.039
		9 weeks	1.217	1.968
Methyl phenyl urethane (8/8/23)	0.3761	1 day	0.1422	1.983
		4 days	0.1192	1.781
Acetone	1.050	1 day	0.01621	
		14 days	0.01618	
		28 "	0.01614	
		120 "	0.01572	
	1.045	1 day	0.02047	
		14 days	0.02046	
		28 "	0.01999	
Methyl ethyl ketone	0.8303	1 day	0.01368	
		56 days	0.01347	

position one to another so that the order of the solvents is approximately the same at every age. Furthermore, this same relative order of the absolute values of the slopes is maintained at age 168 days. This again is substantially the order of the initial values of the slopes in various solvents and is the order in which we would classify the solvents from good to bad.

12. *Ageing has a high temperature coefficient and still occurs at temperatures below the point of solidification of the solvent.*

Squance carried out measurements at 90° in which ageing is very much greater and much more rapid than at 50°. Ageing has thus a high temperature coefficient by Table XV due to Edwards at 25°, where the fall in viscosity is very slow.

Ageing still occurs when the solutions are allowed to solidify through crystallization of the solvent. When such solutions are only slightly below the melting point, the ageing may sometimes even be intensified; it is probable that in such cases only the free solvent and not that associated with the nitro cotton has crystallized. These remarks are illustrated by the data obtained by Smith, Table XVI.

TABLE XVI

Viscosity slopes of solutions of nitro cotton prepared in benzophenone (0.45%) and in o-tolyl urethane (0.36%) at 55° and measured at 55° but kept under various conditions at lower temperatures

Treatment	Benzophenone Viscosity slope	o-Tolyl urethane Viscosity slope
Measured at age 24 hrs. at 55°	(1.55)	1.66
Kept undercooled at 40° for 13 days	1.07	1.47
Kept crystallized at 40° for 13 days	1.48	1.394
Soln. kept crystallized at room temperature for 13 days	1.50	1.65

Discussion.

Almost invariably the viscosity of a cellulose ester changes on keeping even under constant conditions. Our work has been confined to temperatures above those at which gelatinisation of a fluid solution of nitro cotton takes place so that in all cases we observe a decrease in viscosity with age. The change in slope means a great change in viscosity so that 1% solution of nitro cotton that has been kept at 55° for a few months has a viscosity only a few per cent of its original value, a 1% solution of nitro cotton originally has a viscosity of between 7 and 100 times that of the solvent but finally it is not more than a few times that of the solvent even in the poorer solvents and in the best solvents it may exceed that of the solvent by as little as 20%.

There must be at least three aspects of the ageing process. The first is the increase in viscosity noted by other workers, but not observed in our work (even in measurements commencing at age 3½ hours), probably owing to our insistance upon obtaining homogeneous sols before measuring viscosity. This would undoubtedly be the breaking up of the finely divided suspension of nitro cotton just sufficiently to form a true sol. The other two influences to be distinguished are the extent to which the viscosity is ultimately decreased and the rate at which the various solvents are able to effect this end. In confining the discussion to these three factors it is assumed that there is no chemical change occurring such as denitration through decomposition or nitration of the solvent.

Both viscosity and slope fall rapidly at first but apparently without reaching any definite end point. The absolute differences in slope and viscosity are greatest within the first week and least after long ageing; but the relative values of slope; that is, the ratios between slopes for various solvents are greatest after long ageing, whereas the ratios between solutions of highest and lowest absolute viscosity show no great regularity but are of the same order of magnitude throughout.

Inspection of Fig. 5 shows that the curves for slope exhibit but little confusion, there is comparatively little crossing. It seems a fair general description of the curves to say that viscosity in the solvents exhibiting the highest initial slopes (the poorer solvents) changes most but does so more slowly, in the best solvents, with the least initial slopes it changes most rapidly but has not so far to go.

It is important to note that the same behavior was observed and the same conclusions drawn for all the previous data obtained from work with less pure samples of solvent including those whose impurities made them into good solvents.

All this fits in with our interpretation that the best solvents are those which, right from the beginning, most thoroughly and quickly disintegrate the colloidal structure and reduce the aggregates to the smallest dimensions. The poorer solvents are those which are only partially successful in dissolving the bonds between the micelles of which the colloidal aggregates are built up. This distinction between the solvents persists and is even more marked at the end than it is initially. According to our view these larger loose aggregates immobilised a greater proportion of solvent and produce higher apparent viscosity. The slowness of the ageing effects we ascribe to the smallness of the residual affinity effects involved.

Conclusion.

Throughout all our work at 55° whether with pure or impure solvents, these solvents in which the viscosity slope was initially greatest, change most with time, but even after an indefinite period have relatively a much greater viscosity slope than the best solvents and solvent mixtures. The viscosity changes are enormous but they are in accordance with the hypothesis that the best solvents are those which most quickly and effectively resolve the colloidal aggregates into the smallest particles. The higher the temperature the greater the amount of degradation and the more quickly it takes place but apparently no definite end value is attained.

III. The effect of Preliminary Treatment of Nitro Cotton with Acetone or Aqueous Acetone. (A method by which the viscosity of nitro cotton can be enhanced)

J. Duclaux and Mme. Wollman[1] when fractioning a commercial nitro cotton in acetone by progressive addition of water, observed that the slope of the relative viscosity for any one specimen of nitro cotton was approximately the same in various solvents. Thus the slope was 0.3 within 5% for a particular sample of nitro cotton in the following five solvents:— ethyl acetate, methyl alcohol, acetone, methyl formate, iso-butyl formate. It will be noted that all these are good solvents and should give comparable slopes. Whilst it is correct to point out the difference between the slopes caused by extreme varieties of nitro cotton according to Duclaux and Wollman, it is definitely wrong to generalize and say that the slope is independent of the solvent. With the purer solvents we have used, the range of slope is at least four-fold and with impure solvents at least 20-fold. The whole of our work consistently shows that when the relative viscosity is carefully measured under standard conditions it depends greatly upon the nature of the solvent, thus definitely disproving the suggestion of Duclaux and Wollman.

Duclaux used the Arrhenius formula, and his constant K is the viscosity slope as used in the present paper but multiplied by 100. There is no indication that he took effective measures completely to remove the acetone from the precipitated samples of nitro cotton which were under test.

Duclaux found that by this progressive fractionation he obtained a series of samples of nitro cottons whose viscosity slopes measured in acetone ranged from 3.70 down to 0.08. (Ours is about 1.3). All these fractions had the same nitrogen content and gave the same proportion of ash and differed only in the degree of colloidal dispersion. Duclaux was convinced that his separate fractions pre-existed in his original nitro cotton. However, we shall show that the very procedure of fractionation, and the manner in which it is carried out may appreciably affect the viscosity of the material obtained and may be used either to diminish or to enhance the viscosity and still more solubility. Duclaux's demonstration that all the fractions have the same ash and nitrogen content and differ only in size of particle and viscosity affords strong support for the theory of neutral colloids and the interpretation of viscosity put forward in the following paper. Duclaux found that the coarsest particles were the first to be precipitated and were those which gave the highest viscosity and the parallelism between these three properties also in accordance with the point of view here maintained.

1. *Experimental.*

From 55.3 grams of nitro cotton Duclaux obtained three fractions of 21 grams, 23.5 grams and 8 grams by adding various acetone-water mixtures to the solution of nitro cotton in acetone. R. T. Dale worked under the same quantitative conditions with Nobel's nitro cotton and practically the whole 55.3 grams precipitated out as a gelatinous first fraction. A remaining fraction of about 1 gm. formed a milky suspension and could be separated only by using a Chamberland filter.

---

[1] Bull., **22**, 414 (1920).

The precipitated nitro cotton was washed with distilled water until all the smell of acetone had vanished, and was then kept in repeated changes of distilled water. The first addition of water changed the gelatinous precipitate to a tough, white coherent solid. Finally the precipitated nitro cotton was dried in an air oven for three hours at 60° and left in a desiccator for six months. A sample of the original nitro cotton was dried for twelve hours at 60°C. Solutions could not be made under standard conditions at 55°. In ethyl phthalate it was necessary to place the solutions in the shaking machine at 88° for about 40 hours. Such solutions when measured at 55° gave a viscosity slope 11% *higher* than that of the original nitro cotton. Similarly formanilide solutions about a fortnight old at 55°, which had had 163 hours standard shaking were about 25% more viscous than similar solutions made from original nitro cotton.

Edwards recovered nitro cotton not by precipitation but merely by evaporating an acetone solution to dryness. After heating at 60° for 10 days it still showed an increase over the original weight of 0.2%. It gelatinised but did not dissolve in benzyl phenyl urethane even after shaking for 14 days at 55°. A second sample which was prepared by evaporation at room temperature required five days of shaking at 55° to dissolve (incompletely) in benzyl phenyl urethane. A third sample prepared by precipitation like Duclaux's after a fine grinding could be dissolved in benzophenone, phenyl urethane or benzyl formanilide with a couple of days shaking at 55°.

Smith prepared several samples of recovered nitro cotton by very gradual precipitation using several procedures. The third specimen was prepared by adding water drop by drop to a filtered 5% solution in acetone, the mixture being continuously agitated. The fine precipitate was dried in vacuo at room temperature for a week then at 60° for 3 hours. The various recovered nitro cottons were measured in ethyl formanilide, formanilide and phenyl urethane, the third specimen giving distinctly more viscous solutions than the original nitro cotton. Recovered nitro cotton had undergone about four days wet heating and one day's dry heating at 60°. The following table is particularly interesting because it shows the viscosities observed when these nitro cottons were dissolved in acetone, the solvent from which they had originally been precipitated.

Table XVII

Times of flow of solutions of 2 gm. nitro cotton in 100 ccs acetone (prepared at room temperature) shaken until solution is complete (about 3 hours) maintained for 23 hours at 55° and measured at 25°.

Series	a	b*	c*
Recovered nitro cotton (1)	666.8	679.0	694.6
Recovered nitro cotton (2)	802.4	—	—
Recovered nitro cotton (3)	1367.4	1274.6	1312.0
Original 3 hrs. heated N. C.	555.8	661.2	667.6

* In series b and c a different sample of acetone was used.

(c) *Discussion.*

The outstanding result is that nitro cotton recovered from solution in acetone is much more difficult to dissolve than the original nitro cotton whether the nitro cotton has been recovered by precipitation or by evaporation of the acetone. The length of time required for dissolving any one specimen of different solvents is roughly parallel with the magnitude of the usual viscosity slope and only the best solvents can dissolve recovered nitro cotton within 24 hours. This difficulty in dissolving must be largely a physical effect due to the less fine state of subdivision of the recovered as compared with the original nitro cotton. In other respects recovered nitro cotton is not very different from the original either in absolute magnitude of the viscosity slopes in the various solvents or in the diminution of viscosity with age in these solvents.

The enhanced viscosities observed in several cases particularly in acetone seem to be beyond the possible experimental error. It is puzzling that this effect is most pronounced in acetone; possibly the effect may be explained as being due to a firm re-coupling of colloidal particles or micelles which were separated in the original acetone solution. Removal of the acetone must apparently couple some of the bonds from which it has been split off, in a way somewhat analogous to the coupling one gets in such reactions as that of Fittig. Here however since residual affinity is involved it does not appear necessary that acetone has to be split from both groups simultaneously in order that they should unite. It is quite conceivable that when these coupled particles are again placed in acetone their bonds are not necessarily or immediately reloosened to allow of resolvation. It is possible too that at room temperature a nitro cotton solution may be becoming on the whole less viscous through the colloidal aggregates breaking up at certain junctions whilst simultaneously other bonds in a different part of the micelles are in process of linking up to form new but perhaps smaller colloidal aggregates.[1]

IV. Alcohol as a Solvent for Nitro Cotton

(c) *Experiments at very low temperatures.*

Experiments were carried out by L. E. Smith on the gelatinizing power of alcohol. It was found that the nitro cotton containing 12.1% nitrogen was soluble at room temperature to the extent of 0.35% in 95% alcohol. Experiments were devised to find the solubility of the same nitro cotton at low temperatures in anhydrous alcohol. The alcohol was thoroughly dried and then distilled into tubes already containing the nitro cotton. Solutions of various concentrations were prepared. The tube containing the smallest quantity of nitro cotton was first cooled in a mixture of solid carbon dioxide and ether; and the nitro cotton formed a solid compact mass which could not be broken up by shaking. The other tubes were well shaken before cooling to prevent this from happening. On cooling the second tube containing approximately 0.8% nitro cotton the liquid became more viscous and dissolved the nitro cotton, forming a viscous sol which on warming to room temperature set to a flowing jelly or gel. The change from sol to gel was reversible, for on cooling the gel it reverted to the sol form. Two more solutions showed the same phenomenon. The gels became more turbid as the concentration of the nitro cotton was increased. The solution containing 5% nitro cotton was a stiff very turbid gel. These gels are stable at room temperature and even after a period of 18 months still show the reverse change on cooling. They show the phenomenon of syneresis to a marked degree. It is impossible to measure the actual solubility of nitro cotton under such conditions.

---

[1] Compare the solutions of original N.C. in benzyl formanilide referred to on p. 339

Ether was also tested to see if it also exerted a solvent action on nitro cotton at low temperatures, but without success. A sample of ether which had been in contact with nitro cotton for 18 months showed that it had dissolved only 0.004% of the nitro cotton. According to Kugelmass[1] ether at low temperatures dissolves traces of nitro cotton forming suspensoids showing a blue opalescence. In the case of alcohol he reported a series of distinctly separated layers. Neither of these observations could be confirmed by Smith.

Mardles[2] states that he found with cellulose acetate on simply cooling precipitation took place in some sols. "Schützenberger[3] pointed out that the triacetate of cellulose dissolved in nitro benzene on warming whilst on cooling the solution it was precipitated in a gelatinous form. The method of observing this transition temperature of the dispersion medium from a complete solvent to a partial or non-solvent has been used to appraise the relative solvent powers of liquids for cellulose esters in a research on solvents suitable for aeronautical varnishes, the principle being that the lower this temperature, the better the solvent[4]. However, this cannot be a universal method since in alcohol and in Szegvari's experiment the temperature effect would be upside down.

(*b*) *Experiments with alcohol at high temperatures.*

Mardles[5] states:—"Although a liquid may be a non-solvent of a cellulose ester, at temperatures at and below its boiling point at atmospheric pressure, it often happens, for example with alcohol, benzene, methyl ethyl ketone for cellulose acetate, that it becomes a solvent at higher temperatures. Anhydrous alcohol becomes a solvent for a particular sample of cellulose acetate at 120° and industrial at 100°. Thus alcohol cannot be considered merely as a diluent, since in mixtures, especially when dissociated, it must contribute greatly to the solvent action." The validity of Mardles conclusion evidently requires re-examination in the light of our results with cellulose nitrate and alcohol at high temperatures. Nitro cotton and alcohol were sealed in a glass tube and heated to 100° for two or three hours, but no gelatinisation appeared to take place in this time. The tube was then heated at 120° for upwards of 12 hours and at the end of this time most of the nitro cotton had dissolved leaving a slight residue. The solution obtained was yellow and very mobile even when 10% of nitro cotton had gone into solution. Alcohol containing varying amounts of water also dissolved nitro cotton, but the greater the proportion of water in the mixture the greater the amount of residue and the darker the solution.

---

[1] Rec. Trav. chim., **41**, 751 (1922).

[2] J. Soc. Chem. Ind., **42**, 127T (1920).

[3] Compt. rend., **68**, 814 (1869).

[4] Mardles, Moses and Willstrop: Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.

[5] J. Soc. Chem. Ind., **42**, 128T (1920).

It is obvious that this solvent action is not due to unchanged alcohol alone, but partly to the products obtained by the nitration of the alcohol by the nitro cotton. The solution smelt strongly of esters. The residue was probably nitro cotton but this has not been tested.

(*c*) *Discussion.*

There are very few instances of a gel being formed from a sol on heating, and reforming a sol on cooling. Szegvari[1] thought that he had discovered the first one; namely, nitro cellulose dissolved in a mixture of amyl acetate and benzine (not benzene). This is not so striking as the present case of alcohol, where the possibilities are more limited.

Szegvari set up the *ad hoc* explanation that at lower temperatures the amyl acetate combined with nitro cellulose rather than with benzine, whereas at higher temperatures a compound was formed between amyl acetate and benzine to the exclusion of the former combination. In the present case there is no benzine to compete with the nitro cellulose.

All the experimental observations fit in well with our general working hypothesis which says nothing about association, dissociation and hypothetical combination between solvents but presupposes that certain definite chemical bonds of residual affinity have to be satisfied by combination with appropriate groups of suitable solvents in order that the micelles can be freed from each other. A mixture of suitable solvents is more likely to supply the correct groupings necessary for solvating the different portions of the nitro cellulose molecule. Alcohol by itself is a complete solvent at sufficiently low temperature, but an incomplete one at ordinary temperature owing presumably to de-solvation and relinking of certain bonds at the extremities of the constituent micelles which thereupon are relinked. This again explains the solvent action of "alcohol" at extremely high temperatures where the nitrogen content of the nitro cellulose is lowered and an ethyl nitrate appears in the solution.

To sum up, anhydrous alcohol is a complete solvent for our nitro cotton at very low temperatures but at ordinary or high temperatures admixture with a supplementary solvent such as ether or an ester is essential. The sol-gel transformation in anhydrous alcohol is completely reversible.

V. Properties more or less parallel to Solvent Power

It is convenient to summarize the available information with regard to properties which we have found more or less parallel to solvent power[2]. Good solvents unite strongly with nitro cotton, not being completely recovered either by heat or extraction; they have low melting points, relatively low viscosity, abnormally slow rate of crystallization, and their rate of crystallization is more affected by the addition of nitro cotton. The apparent viscosity of a fresh solution divided by that of the solvent is least for the best solvents steadily increasing up the worst solvents. Poor solvents require much greater time to prepare homogenous solutions, their viscosity changes most on ageing, but the change is slower. All adjustments of equilibrium with nitro cotton, such as extraction or degelatinization, seems to be slow with poor solvents, provided that they are actually capable of dissolving or gelatinizing nitro cotton. Within any homogeneous series the lower the molecular weight the greater the solvent power. Relatively small amounts of good solvents have to be added to non-solvents to give them power of dissolving nitro cotton and the best solvents stand most dilution before losing this power; however, this depends to a certain extent upon the complementary nature of the particular solvent and non-solvent chosen. The best solvents are adsorbed to the largest extent and are combined most firmly. Solvents evolve much greater heat of reaction with nitro cotton than do non-solvents. Finally, admixture with suitable complementary substances greatly enhances solvent power.

---

[1] Kolloid-Z., 34, 34 (1924).

[2] For a theoretical definition of the term "solvent power" see VIII. General Conclusion, at the end of this paper. A technical definition may be based upon the uniform appearance and ease of pressing of nitro cotton gelatinized under manufacturing conditions, but this is not quite the same as the insistance that the solvent itself in sufficient quantity produces a fluid sol.

Sproxton[1] suggests from methods of measuring solvent power:—

1. First and most sensitive, apparent viscosity, which is the subject matter of the present paper.

2. Second, the so-called transition temperature; that is, the degree to which a sol can be cooled before solidification, but there is a radical objection to it because some systems show the temperature upside down, for example it is on cooling not on heating that alcohol forms sols.

3. Third, his supposedly least dependable criterion, the amount of diluent which can be added. Mardles has again made great use of this, calling it solvent power and occasionally varying the actual diluent employed. The only objection which rises from our conception and which is fully substantiated by L. E. Smith's experimental work (not included in this paper) is that the result depends upon the complementary nature of the particular diluent and solvent employed. Even the use of a perfect non-solvent if such exists, does not obviate this difficulty since it does not take into account the different kinds of chemical grouping with which various solvents unite.

4. Lastly, measurement of the amount of nitro cotton dissolved from partially soluble esters; that is, a specimen which presumably contains quite different nitro cotton, (not like the very homogeneous specimen we have used).

It is of interest to note that Mardles[2] has met several cases where criteria 1 and 3 conflict; that is, where apparent viscosity does not go parallel with "solvent power." This is only what could be expected in view of the preceding discussion.

---

[1] Trans. Faraday Soc., **16**, Colloid Discussion, 78 (1921).

[2] J. Soc. Chem. Ind., **42**, 210T (1923).

VI. General Summary

1. By taking suitable proportions it is possible to obtain accurate reproducible measurements of the apparent viscosity of nitro cotton in various solvents.

2. Nevertheless, the apparent viscosity cannot be regarded as a true viscosity such as is possessed in an ordinary liquid or solution because experimentally it is found to depend distinctly upon the rate of shear and theoretically it is shown that the viscosity is so great that it must be ascribed to interference between ramifying aggregates of colloidal particles in the solution.

3. A list of the factors which influence the apparent viscosity discussed.

4. It is shown that the period of drying nitro cotton at 60° affects the viscosity of the solutions subsequently made therefrom. The most viscous solutions are those made from nitro cotton which has been heated for less than one day, and the viscosity is progressively less when the preliminary heating of the nitro cotton has been extended to weeks or months.

5. Vigorous shaking of freshly prepared solution diminishes the viscosity apparently by assisting in breaking down residual structures derived from the figures of nitro cotton.

6. The available information with regard to mixtures of liquids whether solvents or non-solvents is reviewed and extended and it is shown that in the vast majority of cases a mixture in suitable proportions is a better solvent than the individual ingredients.

7. Likewise the solvent power of a given material is greatly dependent upon adventitious impurities; the purer sample in general being the least efficient solvent.

8. It is amply demonstrated (contrary to a suggestion of Duclaux and Wollman) that the viscosity of a solution of a particular nitro cotton even when referred to that of the respective solvent depends greatly upon the solvent power of the solvent. The best solvents give the least viscous solutions. Formanilides were better than urethanes or than pure esters.

By various treatments of nitro cotton previously dissolved in acetone—the resultant viscosity of the solutions made therefrom may be affected and even increased. The recovered nitro cotton is far more difficult to dissolve.

10. The viscosity of all solutions of nitro cotton diminishes on keeping at 55° the change being roughly proportional to the logarithm of the time and the slope of the graphs such as would correspond to the viscosity of solutions in the best solvents becoming comparable with that of the solvent in about one year whereas the poorer solvents would take up to 60 years. This so-called degradation is ascribed to progressive dismemberment of the colloidal aggregates into the constituent colloidal aggregates or micelles.

11. It is shown that anhydrous alcohol is a complete solvent for propulsive soluble nitro cotton at low temperatures whereas at room temperature the sol sets to a jelly. This change being reversible indefinitely. The rather imperfect solution at very high temperatures (130°) was shown to be due to the impurities resulting from denitration and decomposition. A complete list

of all the various properties which are more or less parallel to solvent power is given.

12. The following substances have no visible effect upon nitro cotton although it is certain that they all combine with it to various extents: water, benzene, toluene, chloroform, ether, petral, tolyl carbonate, dibenzyl ether.

VII. General Conclusions

The fundamental facts operative in the behavior of solvents and nitro cotton is direct combination between solvent and suitable complementary chemical groups in the nitro cotton. The apparent viscosity of the solutions is almost entirely due to the presence of loose ramifying aggregates of colloidal particles united by local and specific bonds of residual affinity of different kinds and degree. The best solvents are those which most effectively combine with these bonds and by themselves satisfying the residual affinities dismembers the aggregates. Hence, the best solvents yield solutions of the lowest apparent viscosities and mixtures of solvents and even "non-solvents" affording a variety of suitable chemical groups are much more efficient than a single solvent. Recoupling may take place when the proper points on the chemical particles are deprived of their chemical complements; for example, through action of a diluent. It is even possible in this way to increase the viscosity of a nitro cotton. In the transformation from a sol to a solid if the recoupling takes place without appreciable segregation (comparable with the wave length of light), transparency is not affected. In this way coherent films and transparent lacquers are produced. The above theory if correct should be applicable through out the whole subject of colloids.

We have great pleasure in acknowledging the invaluable support of Messrs. Nobel's Explosive Co., Ltd. and the unfailing interest of their scientific staff.

Department of Physical Chemistry,
The University,
Bristol, England.
September, 1925.

ADSORPTION OF ETHYLENE AND HYDROGEN BY ZINC OXIDE, IRON OXIDE, NICKEL AND COPPER*

BY WILBUR A. LAZIER AND HOMER ADKINS

The more recent investigations on the adsorption of gases by solid catalysts have shown that adsorption precedes catalytic activity altho the latter does not necessarily accompany the former. It has been further demonstrated that any change in the extent of one of the manifestations is accompanied by a change of the other in the same direction. For example, Pease and Stewart[1] have shown that poisoning a copper catalyst with mercury or carbon monoxide or deactivating it by high temperatures, not only lowers the activity towards hydrogenation of ethylene but the adsorptive capacity for the reacting gases as well.

It has also been proposed that the course of competing reactions may be determined by the relative adsorption of the reactants or resultants of the reaction in question. The importance of correlating, when possible, data on adsorption and catalysis is thus demonstrated and there are too few examples of these two sets of data available on the same materials. Measurements of the adsorption of hydrogen and ethylene by seven catalysts have been undertaken in connection with a study of the catalytic characteristics of those contact materials previously reported.[2]

Experimental

Apparatus: The apparatus used was a modified form of that described by Pease[1]. The arrangement of the various parts is shown in Fig. 1. A is the catalyst bulb which was of common glass tubing, 1 to 3 cm. in diameter and 6 to 10 cm. in length, depending upon the amount of solid material used in a determination. The bulb was heated by an electric tube furnace not shown in the figure, and was connected to the manometer, B, by means of a glass capillary tube and three-way stopcock. The manometer was equipped with a leveling bulb filled with mercury. The water-jacketed gas burette, C, was of 100 cc. capacity and was also filled with mercury as a retaining liquid. The vacuum line was placed between the gas burette and manometer, and joined these by means of a glass T, all pieces of apparatus being joined by glass seals. Well-fitting glass three-way stopcocks were used between the various parts as shown in the figure. The vacuum line included a small manometer of the closed tube type, making barometer readings unnecessary. The system was exhausted with a Cenco Hyvac pump, capable of attaining a pressure of .001 mm. of mercury although pressure readings could not be made lower than two-tenths of a millimeter. The bulb, D, was of the same capacity as the burette and was used for the storage of gas. The other apparatus shown in the figure was used for the purification of the gases used.

---

* Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin.

[1] J. Am. Chem. Soc., 47, 1329 (1925).

[2] Adkins and Lazier: J. Am. Chem. Soc., 46, 2291 (1924).

[1] J. Am. Chem. Soc., 45, 1197 (1923).

Preparation and Purity of Gases: Hydrogen was obtained by electrolysis of a 15% solution of sodium hydroxide, the electrodes being of nickel gauze. From the generator the gas was conducted through a drying tube filled with calcium chloride and phosphorus pentoxide, and then through a porcelain tube furnace containing copper heated to redness. In this manner the oxygen included in the gas by diffusion was removed by combustion, after which the gas was again dried by passing over phosphorus pentoxide. In order to completely remove air from the system, the pure hydrogen was allowed to flow past the burette for 18-24 hours before the burette was filled. Commercial ethylene was purified by passing through a condensing system immersed in a freezing mixture in a Dewar flask having a temperature of about 20°C. A sample of this gas was 99.6% absorbed in bromine water. Nitrogen was prepared by the usual method of removing the oxygen from air. Carbon monoxide was obtained by allowing formic acid to drop into concentrated sulfuric acid heated to a temperature of 100°.

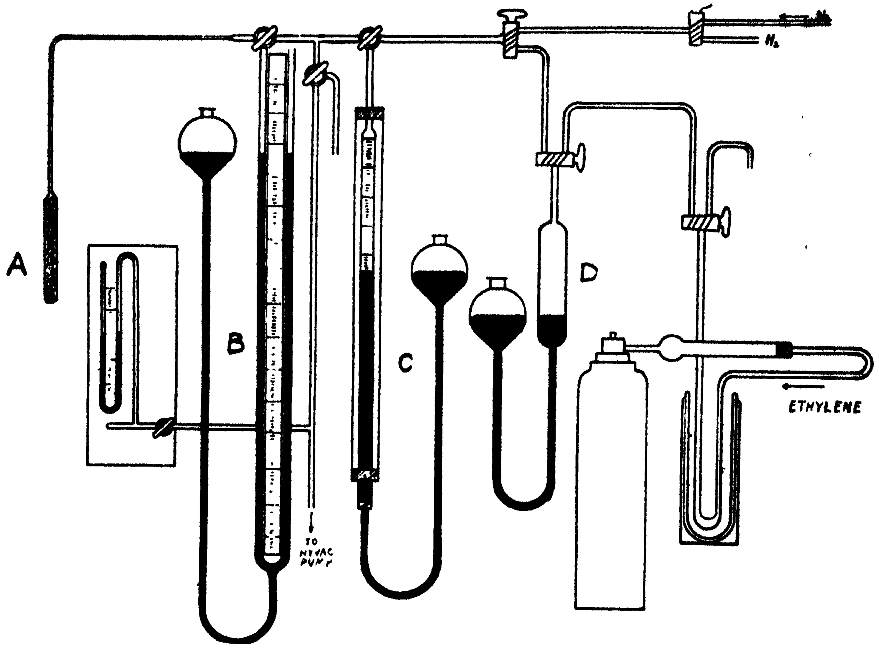


Fig. 1

Apparatus for measurements of adsorption and catalytic activity.

Adsorbents: Seven different adsorbents were used in this work. In each case (except where Merck's granules were used) the oxide was pressed into pellets (3 × 8 mm.) by means of a pharmaceutical tablet machine.

Cupric Oxide ("Ex-nitrate"). Two hundred grams of hydrated copper nitrate was heated in a beaker over a hot plate until the greater part of the water had been expelled and the mass was almost solid, oxides of nitrogen being involved. The mass was cooled, placed in a Pyrex tube open at one end and heated in a furnace at 450° for 4 hours. The black powder was then thoroughly washed with water and ground in a mortar.

Cupric Oxide (*Merck's Granules*). Analysis showed 1.10% Ni_2O_3, 0.21% Fe_2O_3 and 0.47% SiO_2. The material was screened to a uniform size of 30 granules per gram.

Ferric Oxide (*Precipitated*). A hot solution of 100 g. of ferric chloride in 3 liters of water was treated with an excess of ammonium hydroxide. The precipitate was washed four times with three liters of hot water, after which it gave no test for chlorides so was dried at 110°.

Nickel Oxide (Ni_2O_3). Eighty mesh pumice was washed repeatedly with dilute nitric acid and finally with distilled water and then ignited 1 hour over a Bunsen flame. Three hundred grams of nickelous nitrate hexahydrate was melted and 75 g. of pumice stirred into it. This was heated over a hot plate until almost dry and then in a Pyrex tube for 5 or 6 hours at 350° to 400°. The product was found by analysis to contain 38% nickel.

Zinc Oxide (*Ex-hydroxide*). The hydroxide was precipitated from a solution of the sulfate by the addition of the theoretical amount of sodium hydroxide. The precipitate was washed free of sulfate and dried for 24 hours at 110°.

Zinc Oxide (*Ex-zinc isopropoxide*). Dry alcohol—insoluble zinc isopropoxide mixed with sodium chloride was allowed to hydrolyze in moist air. The sodium chloride was then washed out with water and the product dried at 100°.

Copper and nickel were prepared by reduction of their oxides after the bulb containing them had been sealed in place. 62.25 grams of cupric oxide, which yields 50 grams of the metal on reduction was placed in the bulb, sealed to the apparatus and reduced in a stream of dry hydrogen at 200° for 40-60 hours. After reduction was complete as shown by no gain in weight of a calcium chloride tube attached to the outlet of the bulb, the latter was sealed off with the hydrogen still flowing. 26.5 grams of nickelic oxide on pumice which analysis showed would yield 10 grams of the metal was reduced in the same manner but at a temperature of 400°.

A special bulb was devised for the reduction of the same amount of the nickel oxide by alcohol. This bulb contained a perforated core through which the alcohol vapor could penetrate the whole contents of the bulb, thus diminishing the reduction of the oxide which might take place with carbon monoxide, methane, and hydrogen, the products of the reaction of ethanol over nickel. Forty cc. of alcohol was passed through the bulb at 420° in an hour. The bulb was then sealed off.

Ten gram samples of ferric and zinc oxides were used. The greater part of the water of hydration was removed by heating the bulb, while still open at one end, in the furnace at 300°, for 2 hours before sealing on to the apparatus.

Method. Experiments were conducted in cycles of 24 hours, each experiment being begun in the morning and concluded on the following morning. The adsorption bulb was "degased" by exhausting and heating for 3 or 4 hours at 200° in the case of the nickel and copper and at 300° with the oxide catalysts. Temperature control was maintained by means of a Leeds and Northrup potentiometer controller. The current was then turned off, the furnace opened, and the vacuum pump allowed to continue running during the 3 or 4 hours required to cool the contact material down to room temperature. The bulb and manometer and in turn the vacuum line were then shut off from the remainder of the apparatus. The gas burette was then opened to the exhausted tubing and a reading taken at atmospheric pressure, after which gas was admitted to the bulb from the burette. The mercury in the manometer was always adjusted in such a manner that the two columns were level at the same arbitrarily selected point near the top of the scale before volume readings were made on the gas burette. The adsorption of hydrogen by copper was found to proceed rather slowly so that frequent readings and adjustment of the mercury levels were necessary. In all cases the final readings were not made until the following morning. All adsorption determinations and volume readings were made at room temperature and atmospheric pressure. Temperatures and pressures were recorded but since the experimental error was greater than that due to such changes, these factors have been disregarded and the final results calculated from 22° and 740 mm. to 0° and 760 mm. pressure. Duplicate determinations agreeing within .5 cc. were considered satisfactory.

Assuming that nitrogen is not adsorbed, the difference between the volume of nitrogen required to fill the bulb and the volume of any other gas, gave the adsorption of the gas in question. Such an assumption is not quite valid since Benton has found that nitrogen is slightly adsorbed by some oxide catalysts. It is, however, sufficient to give comparative results.

Data on Adsorption

The data obtained in about seventy determinations of adsorption are summarized in Table I. The values given in the Table represent the number of cc. of gas at N.T.P. adsorbed at approximately 22° and 740 mm. pressure by 100 g. of adsorbent. The measurements were made upon both 25 and 50 g. samples of copper from "Merck's Oxide", and upon one of the 50 g. samples which had been oxidized and reduced a second time. 50 g. of copper from copper "ex nitrate" was used. 10 g. samples were used in the case of the other adsorbents. In addition it was found that 100 g. of the iron oxide adsorbed 65 cc. of carbon monoxide.

TABLE I

Adsorption of Gases by Solid Catalysts

Catalyst	Ethylene	Hydrogen
Copper (Merck)	7.2	24.0
Copper (ex nitrate)	2.0	0.55
Nickel (by hydrogen)	70.0	84.0
Nickel (by alcohol)	205.0	61.0
Zinc Oxide (ex hydroxide)	57.0	1.8
Zinc Oxide (ex isopropoxide)	160.0	23.4
Iron Oxide (precipitated)	588.0	0.0

Hydrogenation of Ethylene

Equimolecular mixtures of ethylene and hydrogen were allowed to enter the evacuated adsorption chamber, the catalyst being the same as that used for the adsorption measurements. In the case of nickel (10 g. on pumice, reduced by alcohol at 420°) and Merck's copper (50 g. reduced at 200° with hydrogen) the reaction was so rapid that it was practically (95%) completed before the first (5 min.) measurement could be made. In the case of the nickel the contraction of the gases due to reaction and adsorption was 59.0 cc. as contrasted with an adsorption of hydrogen alone of 6.1 cc. and of ethylene alone of 20.5 cc. The contraction with Merck's copper was 34.0 cc. of the mixed gases as contrasted with an adsorption of 12 cc. of hydrogen and 3.6 cc. of ethylene. Fifty g. of the copper (ex nitrate) only adsorbed or caused to react 3.6 cc. of the mixed gases after 24 hours. The hydrogen adsorption for the catalyst was 0.27 cc. of hydrogen and 1.0 cc. of ethylene when the gases were introduced separately.

Discussion

Certain facts should be noted in connection with the results given above. The nickel, reduced through the use of alcohol, contained carbon which probably affected the amount of gases adsorbed. No means was devised to eliminate this source of error. However the adsorption values were obtained for the sake of tying them up with the measurements in catalytic activity, where carbon was also present. It was impossible to ascertain whether the nickel oxide was completely reduced before the adsorption measurements were made. However, the time of reduction was two or three times as long as previous work had indicated to be necessary, for complete reduction of nickel oxide. It is interesting to note that there was no "induction period" when nickel was used as a catalyst for the hydrogenation of ethylene. Such induction periods have been observed when the catalyst was covered with hydrogen at the beginning of the experiment. In our experiments the nickel was degased before the ethylene-hydrogen mixture was introduced. The experimental results are in accord with Palmer's explanation of the reason for the induction period, i.e. the time necessary for the replacement on the catalyst of hydrogen by ethylene.

The effect of small amounts of nickel in increasing the adsorption of gases by copper and of promoting its catalytic activity is clearly indicated by the behavior of the "copper" obtained by the reduction of Merck's copper oxide granules, as compared to the copper obtained from copper nitrate. It seems probable that the very active "copper" obtained by Taylor from "Kahlbaum's granules" may have contained nickel. (P. 102 of the First Colloid Symposium Monograph, University of Wisconsin, Madison, 1923)

It is evident from an inspection of the results of the adsorption and catalytic activity of these seven catalysts as reported in this paper and elsewhere, that there is a qualitative agreement between the two manifestations of chemical activity, as has been previously demonstrated by the extensive work in the Princeton Laboratories. However, as pointed out by Bischoff[1] and later even more conclusively by Pease and Stewart[2], and by Russell and Taylor[3] there is apparently no quantitative relationship between total adsorption and catalytic activity.

There is not even a qualitative agreement between the relative adsorption of two gases and the relative production of these two gases in catalysis. For example, precipitated zinc oxide is more effective in dehydrogenating ethanol (as compared with dehydrating it) than is zinc oxide from zinc isopropoxide. The former is a much poorer adsorbent for hydrogen that is the latter. It seems certain that the total catalytic activity and the relative activity for different reactions is conditioned not only by adsorption but by the topography of the surface. The question as to whether the effective (for catalysis) portion of the surface is that of very unsaturated atoms[4], or is determined by the spacial relationships of certain atoms[5] will be discussed elsewhere.

Summary

The adsorption of ethylene and hydrogen by seven catalysts has been determined. Data in addition to that already published are given as to the catalytic activity of some of these compounds. The probable effect of 1% nickel in promoting the adsorption and catalytic activity of copper has been pointed out.

Madison, Wis.

---

[1] Bischoff and Adkins: J. Am. Chem. Soc., **47**, 807 (1925).

[2] Pease and Stewart: J. Am. Chem. Soc., **47**, 1239 (1925).

[3] Russell and Taylor: J. Phys. Chem. **29**, 1325 (1925).

[4] Taylor: Proc. Roy. Soc., **108A**, 105 (1925).

[5] Adkins and Nissen: J. Am. Chem. Soc., **46**, 130 (1924).

AQUEOUS SOLUTIONS OF SODIUM SILICATES
PART II. TRANSPORT NUMBERS

BY R. W. HARMAN

In a previous communication[1] the results of the measurement of the electrolytic conductivity of solutions of six sodium silicates of ratios varying from 2:1 to 1:4, have been given. It was there shown that all these silicates are very good conductors in dilute solution, and that in concentrated solution the conductivity decreases as the proportion of silica in the ratio increases.

Earlier investigators such as Kohlrausch[2] and Kahlenberg and Lincoln[3] attributed the high conductivity of solutions of sodium metasilicate to complete hydrolytic dissociation. This view seemed more or less firmly established until measurements of hydroxyl ion concentration by E. M. F. methods by Bogue[4] pointed to a much lower percentage hydrolysis even in dilute solution. Bogue's measurements have been repeated and extended to other ratios and the results will be communicated in a later paper, where it is shown that his conclusions are in the main correct. The conductivity of solutions of various ratios $Na_2O:SiO_2$ cannot therefore be accounted for solely by hydrolytic dissociation, not even in the case of solutions of sodium meta-silicate, where the hydroxyl ion concentration is moderately high. But the ratios 1:2, 1:3, 1:4, etc., have a very low hydroxyl ion concentration, even in dilute solution, and yet their conductivity is quite high. To what is this conductivity due? The conductivity may be accounted for by the presence of a fairly mobile silicate ion, or by assuming that the silicic acid is colloidal and has adsorbed hydroxyl ions. If the latter view were correct, one would not expect the colloidal aggregate to be very mobile, and the osmotic activity of the solution would be abnormally low.

Transport experiments should throw light on this question, and by their means some knowledge could be gained of the kinds of ions and their mobilities. If silicate ions exist in solution, and it seems justifiable in view of conductivity measurements to assume that they do, then their nature must be determined.

When this work was begun, the existence of definite sodium silicates of ratios other than 1:1, i.e. Na_2SiO_3, was very doubtful. No conclusive evidence had been put forward to prove whether they were definite salts or merely mixtures of the metasilicate with silicic acid or caustic soda as the case may be. It was hoped that transport number experiments would produce some evidence as to whether the silica existed as colloid, simple ions, aggregates of simple ions carrying a sum total of their separate charges (i.e. ionic micelles), or as complex ions.

---

[1] Aqueous Solutions of Sodium Silicates, Part I. J. Phys. Chem., **29**, 1155 (1925).

[2] Ann. Physik, (3) **47**, 756 (1892).

[3] J. Phys. Chem., **2**, 77 (1898).

[4] J. Am. Chem. Soc., **42**, 2575 (1920).

While the results do not completely elucidate all these problems, they do yield considerable insight into the nature, complexity, and mobility of the silicate ion.

Experimental

Method.

In solutions corresponding to ratios where hydrolysis has taken place there are three constituents active in carrying the electric current, viz, sodium, hydroxyl, and silicate ions. In such cases the only method likely to yield complete and reliable results is the original analytical method of Hittorf. The moving boundary method seems inapplicable to such solutions containing three kinds of ions, as the boundary formed by the more slowly moving anion would be disrupted by the quicker moving anion, even if a suitable reference substance could be found which did not coagulate or otherwise interact with the silicate solution.

This method could probably be used to determine the transport number of the sodium and the hydroxyl ions, but as the main object of these experiments was to investigate the silicate ion, the moving boundary method was deferred, though it is hoped to develop it later. Other methods of determining the transport number such as by E. M. F. measurements of cells with and without transport, or by gravity and centrifugal cells[1] are also of very doubtful or difficult application in these solutions.

By the analytical method the change in concentrations of sodium and silica at the electrodes may be determined accurately, but unfortunately it is impossible by this method to determine the transport number of the hydroxyl ion directly. The presence of hydroxyl ions and the fact that hydroxyl ions are formed as a result of the cathode reaction, not only makes the determination of the transport number more difficult, but also increases any inaccuracy in the experimental figures. However, a study of the electrode reactions shows this interference, due to the formation of hydroxyl ions, not to be so serious as might at first sight be expected.

Apparatus.

The apparatus shown in Fig. 1 consists of three U-tubes, the middle one about one-half the depth of the outer ones, the whole apparatus being of uniform bore throughout to avoid local heating and convection currents. It was made of resistance glass with ground-glass joints at E and F, so that the middle U-tube could be disconnected from the other two. The outer U-tubes were closed by ground-glass stoppers at A, B, C, and D, those at A and D being hollow and terminating in a tap to allow gas evolved during the experiment to escape. The electrodes of platinum were about 1.5 cm. square and were sealed in through the hollow stoppers A and D. The capacity of the apparatus was about 350 cc. During an experiment the apparatus was immersed in a water thermostat electrically heated and regulated to 25°C. ± 0.01.

The apparatus was cleaned with caustic soda and chromic acid immediately before and after use, no silicate solution ever being allowed to evaporate in it, as it would then have been most difficult to clean thoroughly.

---

[1] Cf. Tolman: Proc. Am. Acad., **46**, 110 (1910).

A current of from 12-20 milliamps, at 55 or 110 volts was passed through the solution for from 2½ to 3 hours according to the strength of the solution. Two silver coulometers, well insulated, were included in the circuit to detect any leakage of current, and to measure the current used. These coulometers agreed within 0.01%.

At the end of an experiment, the solution was divided into five portions shown by dotted lines on the figure, A, AM, M, CM, and C of weights 100, 50, 50, 50 and 100 grams respectively. The taps at A and D being closed, the stoppers B and C were alternately removed and the portions AM and CM withdrawn and transferred to weighed flasks by means of a pipette with an upturned tip, shown in Fig. 1. This was done while the apparatus was still in the thermostat, the tip of the pipette being kept just below the surface of the liquid which was being withdrawn. This prevented any mixing of portions A, M, and C, either by currents set up due to removal of a portion, or by shaking during removal from the thermostat. The apparatus was then taken out of the thermostat, disconnected, the joints freed from grease and portions A, M, and C transferred to weighed flasks. These five portions and a sample of the original were then set aside for analysis.

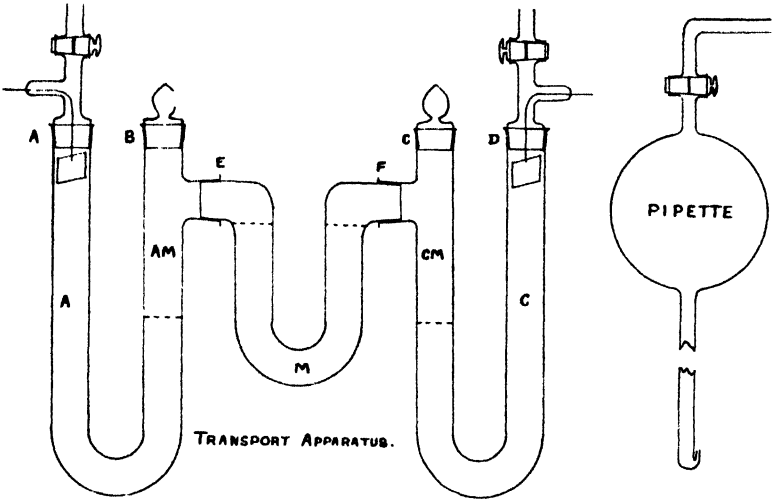


FIG. 1

The solutions used were prepared in a manner similar to that described in Part I, on preparation and conductivity. As there, the term ratio denotes $Na_2O:SiO_2$ in equivalent proportions.

Analysis.

The five portions and the original solution were analysed for both sodium and silica. The procedure strictly followed in each analysis was that given by Hillebrand in his Monograph on "The Analysis of Silicate and Carbonate

Rocks", Bulletin 700 of U. S. Geological Survey, 1919. The solution was evaporated twice to complete dryness with HCl, and the silica ignited and weighed. This silica was then volatilised with HF and the residue weighed. This residue, however, was always practically negligible. The main errors to be guarded against in determining the silica are:—

(1) Incomplete removal from solution owing to an insufficient number of evaporations to dryness. Two are sufficient in the case of a simple silicate such as used here, provided each is a very complete evaporation to dryness.

(2) Failure to remove particles of silica from the evaporating dish. This error may be quite large but can easily be avoided by wiping the dish with a piece of moist filter paper which is then added to the silica to be ignited.

(3) Improper ignition. The error here may vitiate the whole experiment. It is best to begin the ignition with a bunsen flame about the size of an ordinary match flame, gradually increasing it so that the paper distils as a tar on to the crucible lid and finally disappears. If at any time the escaping gases should catch fire, the experiment is quite worthless, owing to the fine particles of silica being carried away by the draught. Finally ignite in a Meker burner till constant weight is obtained—usually half to one hour. The silica residues were always snow white.

By using these and the usual precautions, duplicate analyses for SiO_2 agreed within 0.01%.

The sodium was determined as NaCl, due precaution being taken to dry it thoroughly without losing any through decrepitation or volatilisation. Occasionally the water in the solution was determined by Penfield's method, but usually when needed it was found by difference.

The method of analysis outlined above was used throughout the whole of this investigation and so applies to all the other analyses mentioned in the papers on this subject. Since both electrode portions were analysed for both sodium and silica, we obtain two independent measures of the transport numbers for both the sodium and the silicate ions and thus have a valuable check on their accuracy. The middle portion M was in all cases found to be the same as the original solution within experimental error. The changes in Na_2O and SiO_2 content of the portion AM were added to the corresponding changes in portion A to give the total change at the anode, and similarly for CM and C to get the total change at the cathode.

In expressing the results of the analyses, the sodium weighed as NaCl has always been calculated as Na_2O for convenience in comparison with SiO_2, since the comparison of the two oxides represents a direct measure of the composition of the silicate and this is the basis of the system of nomenclature used. The change in sodium content in the electrode portions has therefore been expressed in these experiments as a change in Na_2O content.

TABLE I

No. of Expt.	Ag dep.	Portion	Analysis %Na_2O	Analysis %SiO_2	Total change in gms. Na_2O Loss	Total change in gms. Na_2O Gain	Total change in gms. SiO_2 Loss	Total change in gms. SiO_2 Gain	Transport Numbers. N_{Na}	Transport Numbers. N_{SiO_2}
1	.3650	orig.	6 331	5 790						
		A	6 313	5 816	.023			017	.22	.166
		M	6 336	5 799						
		C	6 369	5 781		.033	018		32	176
									27	17
2	2054	orig.	3.080	2 854						
		A	3 051	2 862	.027			008	.36	13
		M	3 073	2 854						
		C	3 106	2 846		.028	.008		36	13
									36	13
3	3488	orig.	3072	2918						
		A	2755	3122	.0277			.01706	28	175
		AM	.3038	2936						
		M	3038	2920						
		CM	3127	2903		.0343	01797		34	184
		C	3475	2706						
									31	18
4	2742	orig.	3 060	5 940						
		A	3.000	6 060	.0378			.0690	48	90
		M	3 063	5 945						
		C	3 112	5 833		.0294	0672		35	87
									42	88
5	3238	orig.	1.450	2 850						
		A	1 418	2 916	.0336			.0566	36	63
		AM	1 463	2 881						
		M	1 455	2 859						
		CM	1 477	2.839		.0312	.0612		34	78
		C	1 487	2 787						
									.35	70
6	2690	orig.	3251	6342						
		A	2638	7422	.0551			.08159	65	98
		AM	3088	6346						
		M	3256	6339						
		CM	3414	6241		2328	.05822		25	75
		C	3447	5693						
									45	87
7	.2752	orig.	2 946	8 356						
		A	2 919	8 482	.0374			.1096	47	1 43
		AM	2 929	8.380						
		M	2 950	8 360						
		CM	2 961	8 332		0248	.0989		32	1 29
		C	2.969	8 273						
									40	1 36
8		orig.	1.550	4 325						
		A	1 520	4 535	.0302			.09759	45	1.50
		AM	1 538	4.364						
		M	1.548	4.329						
		CM	1.560	4.295		.0304	.1046		45	1 60
		C	1 574	4 238						
									.45	1 55

TABLE I (continued)

No. of Expt.	Ag dep.	Portion	Analysis		Total change in gms. Na_2O		Total change in gms. SiO_2		Transport Numbers.	
			%Na_2O	%SiO_2	Loss	Gain	Loss	Gain	N_{Na}	N_{SiO_3}
		orig.	2.806	10 30						
		A	2.834	10 43	.0261			.110	52	2 25
		AM	2 802	10 35						
9	.1748	M	2 808	10 31						
		CM	2.813	10 26		.0275	.117		55	2 39
		C	2 837	10.19						
									53	2 32
		orig.	.3560	1.205						
		A	3132	1 479	.0345			.2168	.42	2.76
		AM	.3510	1 180						
10	.2820	M	.3563	1 207						
		CM	.3620	1.238		0377	.1674		46	2 13
		C	.3982	1 021						
									44	2 44

Calculation of Transport Numbers.

Assuming in the first instance the presence of only Na^+, OH^-, and SiO_3^{--} ions in the solutions, and setting 1 Ag^+ equivalent to 1 Na^+ and to $\frac{1}{2}$ SiO_3^{--}, the transport numbers of the sodium and silicate ions have been calculated thus:—

$$\text{T. N. sodium} = \frac{\text{total change in weight of } Na_2O \text{ content}}{\text{weight of } Na_2O \text{ equiv. to Ag deposited in coulometer.}}$$

$$\text{T. N. Silicate} = \frac{\text{total change in weight of } SiO_2 \text{ content}}{\text{weight of } SiO_2 \text{ equiv. to Ag deposited in coulometer.}}$$

The T. N. of the hydroxyl ion has been determined by subtracting the sum of the transport numbers of the sodium and silicate ions from unity.

This method of calculating the transport number of the silicate ion ignores the possibility of the existence of $HSiO_3^-$ ions, and also of more complex anions containing more than one mol SiO_2 per 2F. These points will be considered later.

Results.

Table I contains the results of 10 experiments on ratios 1:1, 1:2, 1:3, and 1:4 at concentrations approximately 1.0N_w, 0.5 N_w and 0.1N_w. In the columns headed "analysis" are given the percentages of Na_2O and SiO_2 found in the several portions. The next four columns give the actual loss or gain of Na_2O and SiO_2 in grams, obtained by multiplying the percentage change by the weight in grams of the portion. The increases in the percentages of Na_2O and SiO_2 in the portions analysed caused by the escape of hydrogen from the cathodic solution and of oxygen from the anodic solution introduce corrections which are within the limits of experimental error. The weights of the different portions were between 80-100 grams for A and C, and between 45-55 grams for M, AM, and CM, depending on the density of the solutions.

Table II contains the results collected in a more convenient form for comparison.

TABLE II

No. of Expt.	Ratio	Approx. N_w		n_{Na}	n_{SiO_3}	By diff. n_{OH} $= 1-(n_{Na}+n_{SiO_3})$
1	1 : 1	2.36		.27	.17	.56
2	1 : 1	1.0		.36	.13	.51
3	1 : 1	0.10		.31	.18	.51
			Mean	.31	.16	.53
4	1 : 2	1.0		.42	.88	
5	1 : 2	0.5		.35	.70	
6	1 : 2	0.1		.45	.87	
			Mean	.41	.82	
7	1 : 3	1.0		.40	1.35	
8	1 : 3	0.5		.45	1.42	
			Mean	.43	1.38	
9	1 : 4	1.0		.53	2.32	
10	1 : 4	0.1		.44	2.44	
			Mean	.48	2.38	

Accuracy of Results.

The analyses are correct to within less than 0.1% both for Na_2O and SiO_2, but even this high accuracy in the analysis represents a considerable error where the total change in the electrode chamber is of the order of 1%, as is the case with Na_2O. In the case of the silica, especially in the higher ratios, this is proportionally lower. If only one electrode portion had been analysed, this degree of accuracy would not have warranted much value being placed on the transport numbers, but since both electrode portions were analysed, we obtain two transport numbers in each case which serve as a very useful check. In the majority of the experiments it can be seen that the two transport numbers differ from the mean by about 10% for the sodium ion, and by from 2 to 5% for the silicate ion. Unfortunately the accuracy of the results does not warrant any quantitative conclusions being drawn as to the variation of the transport number with concentration, but it is sufficient to show that the transport number does not vary greatly over the range of concentrations investigated.

Discussion of Results.

Considering first the ratio 1:1, i.e. sodium metasilicate, it is seen that the mean of the six values of n_{Na} is 0.31, of n_{SiO_3} 0.16, and of n_{OH} 0.53. The proportion of the current carried by the silicate ions is very small, being only about one-half that carried by the sodium ions, while over one-half the total current is carried by the hydroxyl ions. This latter result was to be expected, since E. M. F. measurements show that 10 to 30% of the silicate is hydrolysed according to the concentration, and the hydroxyl ion moves four times as fast as the sodium ion. In caustic soda n_{Na} is 0.2, and n_{OH} is 0.8; therefore the present result, where n_{OH} is not even double n_{Na}, shows that the concentration of the hydroxyl ions is not nearly equivalent to that of the sodium ions.

From the results of measurements of OH ion concentration, Na ion concentration, and total ion concentration as found from freezing point lowering, all to be communicated later, it will be seen that in ratio 1:1 the concentrations of the ions are approximately in the proportion Na:SiO_3:OH = 8:3:2, calculated by assuming the laws of ideal solution to be applicable. Taking the T. N. of an ion to be proportional to its mobility and to its concentration, this makes the mobility of the simple silicate ion equal to 70. The value 60 was deduced as the mobility of the silicate ion from the equivalent conductivity at infinite dilution.

The T. N. of sodium metasilicate shows no evidence whatever of any complex silicate ions or of micelle formation. If the silica is colloidal with OH ions adsorbed, such a high mobility as 70 would not be expected, as hitherto measurements have shown that such colloidal particles have a mobility approaching that of the slowest moving ions.

When we look at the results obtained with ratio 1:2, 1:3, and 1:4, we at once notice the very high transport numbers of the silicate anions. They are for ratios 1:3 and 1:4 much greater than unity. The average value for ratio 1:2 is 0.88, for ratio 1:3 1.44, and for ratio 1:4 2.38, while the T. N. of the sodium remains much the same, about 0.45 in each case.

Further, the T. N. for the silicate ion is approximately twice that of the sodium ion in ratio 1:2, three times in ratio 1:3, and four times in ratio 1:4. This high T. N. for the silicate ion at once points to the fact that the anion cannot possibly be the simple ion SiO_3^{--}, nor in fact should we expect it to be. These high transport numbers were obtained, it must be remembered, by assuming the anion to be the simple ion SiO_3^{--}.

This high T. N. may result from the following causes:—

(1) The anion may be a solvated aggregate of simple SiO_3^{--} ions, carrying a charge equal to the sum of the total charges on the separate ions, or a solvated aggregate containing more than one mol SiO_2 per divalent charge, these aggregates splitting up on dilution.

(2) The anions may be definite ions more complex than the simple SiO_3^{--} ion, i.e. definite salts of the formulae given below may exist:—$Na_2(SiO_3.SiO_2)$, $Na_2(SiO_3.2SiO_2)$ etc., which ionise to give definite divalent silicate ions of the formulae:—$(SiO_3.SiO_2)^{--}$, $(SiO_3.2SiO_2)^{--}$ etc.

Both in the case of the existence of aggregates and of definite anions, further experimental results, other than those from conductivity and transport number measurements, are required in order that their constitution may be conclusively proved. The decision as to which formation is the more probable will therefore be postponed until the results obtained by other lines of investigation have been communicated and discussed. It is evident, however, that the method of calculation already given for the transport numbers in the case of ratios 1:2, 1:3, and 1:4, is in error and must be modified to the following expression:—

$$\text{T. N. silicate ion} = \frac{\text{total change in weight of silica}}{\text{N} \times (\text{weight of SiO}_2 \text{ equiv. to Ag deposited in coulometer})}$$

where N is the number of mols SiO_2 per divalent charge (2F) of the anion, and the weight of "SiO_2 equivalent to Ag deposited" is calculated as before from the relation, 1 Ag. equivalent to $\frac{1}{2}$ SiO_2.

Since in ratios 1:2, 1:3, and 1:4, the T. N. previously calculated is approximately equal to the T. N. of the sodium ion multiplied by the ratio, it seems that here is no chance relationship, and since also, from the equivalent conductivity at infinite dilution, the mobility of the silicate anion or aggregate, at least in ratios 1:3 and 1:4, is approximately equal to the mobility of the sodium ion, it appears justifiable to put N equal to the molar ratio SiO_2/Na_2O in the solution (average value of N).

When the transport numbers are so calculated, we get the values given in Table III, the results for sodium metasilicate being also given for comparison. The first column N contains the number of equivalents of SiO_2 per Faraday, i.e. the number N in the expression above.

TABLE III

N	Ratio	n_{Na}	$n_{sil.}$	$n_{OH} = 1 - (n_{Na} + n_{sil})$
1	1 : 1	.37	.16	.53
2	1 : 2	.41	.41	.18
3	1 : 3	.43	.46	.11
4	1 : 4	.48	.59	—

Thus calculated, we see that the values of the T. N. for the sodium and silicate ions do not total unity in ratios 1:2 and 1:3, the differences being respectively 0.18 and 0.11, which are presumably the values of the T. N. for the hydroxyl ion. This hydroxyl ion, although present in small amounts, is so much more mobile than the others that we should expect its T. N. to be something of this order, especially in ratio 1:2. In ratio 1:4, the hydroxyl ion concentration is practically negligible and from Table III its transport number is zero.

The transport numbers of the sodium and silicate ions would be approximately the same in ratios 1:2, 1:3, and 1:4, if no hydroxyl ion were present, and since the former ions are present in nearly equivalent amounts, we may conclude that their mobilities are nearly the same, probably that of the silicate ion a little higher in 1:3 and 1:4. This is in agreement with the values of mobilities calculated from conductivity experiments. The fact that the mobilities of these silicate ions are nearly all the same, even though the anion in 1:4 is more complex and so larger per charge of electricity, is probably due to hydration effects, as it has been shown that the more complex the ion the less it is isolated

Summary.

1. Transport numbers of sodium silicates of ratios 1:1, 1:2, 1:3, and 1:4 at concentrations ranging from 0.1 to 2.0 N_w have been measured by the Hittorf method, both electrode portions being analysed for both sodium and silica.

2. Ratio 1:1 evidently ionises to Na^+, OH^- and SiO_3^{--} ions; n_{SiO_3} is small, n_{OH}, found by difference, is large.

3. In ratios 1:2, 1:3, and 1:4, the T. N. of the silicate ion is high, and the silicate anion contains more than 1(SiO_2) per divalent charge; the average number of mols SiO_2 per divalent charge being equal to the ratio.

4. The mobility of the SiO_3 ion in ratio 1:1 is about 70. In ratios 1:2, 1:3, and 1:4, it is approximately equal to that of the sodium ion, thus agreeing with mobilities calculated from conductivity experiments.

5. In ratios 1:2, 1:3, and 1:4, the silicate anion is not the simple SiO_3^{--} ion, but is either an aggregation of simple silicate ions with or without colloidal silica, or a definite complex silicate ion.

I wish to thank the Commissioners of the 1851 Exhibition for a research scholarship which has enabled me to carry out this work, and to express my gratitude to Professor Donnan, at whose suggestion this investigation was undertaken, for his constant kindly interest and advice.

The William Ramsay Laboratories of
Inorganic and Physical Chemistry,
University College, London.
December 1, 1925.

THERMAL ANALYSIS OF THE SYSTEM BORON TRIFLUORIDE-HYDROGEN SULFIDE

BY ALBERT F. O. GERMANN AND HAROLD SIMMONS BOOTH

Since the discovery by Friedel[1] in 1875 of the compound $(CH_3)_2O . HCl$ much interest has attached to the study of molecular combinations between gases. Practically, this discovery was less amazing than the similar discovery by Priestley a century before that gaseous ammonia combines with gaseous hydrogen chloride to form a solid, $NH_3 . HCl$. But the experimental difficulties of assigning a formula to Friedel's compound were tremendously greater than those surrounding the other, which was a well-known compound, whose composition was made evident by the new method of preparation. Since the discovery of Friedel's compound, and his classic research into the nature of the compound, other methods have been developed which permit the detection and formulation of even unstable addition compounds between gases, by methods that are much simpler than those carried out by Friedel. Reference may be made, for example, to the methods used by McIntosh[2] and his co-workers, by Bagster[3] and by Baume and his co-workers[4] for determining the existence and composition of addition compounds by thermal analysis.

In the study of the properties of certain halide gases, the problem of preparing these gases in a high degree of purity confronted us. The best methods of accomplishing this involve the preparation of the desired gas

(a) in vacuo,
(b) from the purest materials,
(c) by a method involving no other volatile products,
(d) a preliminary purification of the gas from possible impurities by chemical means involving a gas absorption train,
(e) condensation of the gas to a liquid, followed by a series of careful fractional distillations, and
(f) if practicable, fractional crystallization.

In spite of all these precautions, however, some impurities are very difficult to eliminate; for example, different investigators have found it diffiult to eliminate from hydrogen chloride some impurity which imparts a rose color to the frozen gas[5]. On the other hand, Inglis[6] found, in a study of chamber gases, that on certain occasions some impurity imparted a red color to the frozen gas, usually white; on these occasions he mentions that the flue gases contained a chloride. Briner and Wroczynski[1] observed that when a mixture of hydrogen chloride and nitric oxide is cooled in liquid air, the resulting solid has a wine-red color. Germann and Phillips[2] have observed the production of a similar color with nitric oxide and boron trifluoride; and Germann has found that other halogen-containing compounds, for example phosgene, behave in the same way with nitric oxide at low temperatures, and he has used this property as the basis of a method for detecting nitric oxide in laughing gas. This red color is undoubtedly to be explained by the formation of an addition compound which halogen gases in general form with nitric oxide.

---

[1] Bull. (2) **24**, 160, 241 (1875).

[2] J. Chem. Soc., **85**, 919 (1904); Maass: J. Am. Chem. Soc., **33**, 71 (1911); **34**, 1273 (1912); etc.

[3] J. Chem. Soc., **99**, 1218 (1911).

[4] J. Chim. phys., **9**, 245 (1911); **12**, 206 (1914).

[5] Gray and Burt: J. Chem. Soc., **95**, 1640 (1909); Cardoso and Germann: J. Chim. phys., **10**, 517 (1912).

[6] J. Soc. Chem. Ind., **25**, 152 (1906).

Evidently the tendency of a gas toward compound formation with a given impurity, as well as the formation of constant-boiling solutions, would enhance the difficulty of making a separation of the impurity by fractional distillation. It seemed highly desirable, therefore, to have more information, particularly at low temperatures about the affinities of the gases being studied for other gases, especially those liable to be present as a result of the method of preparation.

Boron trifluoride and phosgene were under investigation at the time these studies were carried out (1919-21), the intention being to determine the weight of the normal liter of these gases; but owing to the removal of one of us from the Morley Laboratory of Western Reserve University, where the investigations were carried out, the program was not completed, except that some preliminary measurements were made in the case of phosgene[3]. In the preliminary study of these gases, it became evident that the elimination of some of the impurities was very tedious. It seemed, therefore, worth while to determine by the methods of thermal analysis as developed by Baume the possible addition compounds formed by these gases with the impurities likely to be present.

In the case of boron trifluoride, the method of preparation involved the action of sulfuric acid on calcium fluoride and boric anhydride. Gray and Burt have shown that in the similar reaction of sulfuric acid with sodium chloride or with ammonium chloride to produce hydrogen chloride a little hydrogen sulfide was always produced; they attributed its formation to reduction of the sulfuric acid during the reaction. The possibility of hydrogen sulfide being produced in the preparation of boron trifluoride due to the presence of small amounts of reducing substances, suggested the investigation of this system.

Preparation of Boron Trifluoride[4]

70 grams of boric anhydride were dissolved with the aid of heat in 250 cc. of concentrated sulfuric acid. Analysis showed that the boric anhydride

---

[1] J. Chim. phys. 9, 116 (1911).

[2] Science, 53, 145 (1921).

[3] Germann and Jersey: Science, 43, 582 (1921); Germann and Smith: Science, 57, 564 (1923).

[4] Gasselin: Ann. Chim. Phys., (7) 3, 9 (1894).

contained 10% of water. In one experiment, the effort was made to get rid of this water, by adding the calculated amount of pyro-sulfuric acid; but the gas obtained, when condensed to a solid, had a bright red color, obviously due to the same impurity, NO, which imparts a red color to solid hydrogen chloride. As the purity of the pyro-sulfuric acid used was questionable, it seemed probable that it might be the source of this impurity; in subsequent preparations, therefore, the fuming sulfuric acid was omitted, and the mixture made up of 300 cc. pure concentrated sulfuric acid, 75 grams boric anhydride, and 200 grams calcium fluoride. Prepared in this way, the gas condensed as a white solid, without a trace of pink color, and melted to a clear limpid liquid. The use of fuming sulfuric acid thus seems inadvisable.

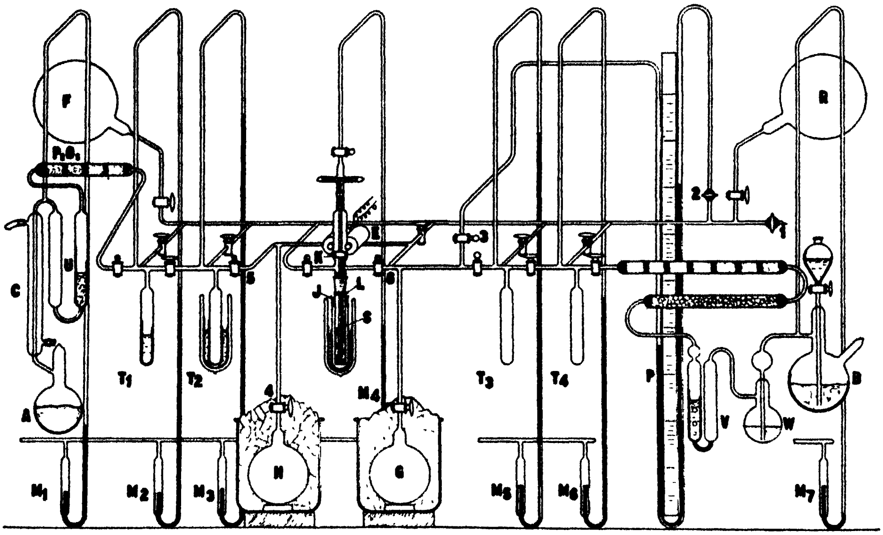


FIG. 1

After cooling the solution of boric anhydride in sulfuric acid, it was mixed with 200 grams of calcium fluoride in a large porcelain mortar, and the mixture, which warms up and froths considerably, was stirred until the gas evolution ceased. The gases given off probably consisted principally of silicon tetrafluoride. The viscous mixture was then transferred to the reaction flask labelled A at the left end of Fig. 1, which shows the arrangement of the apparatus, and the mouth of the flask was then sealed off, as shown.

Flask A communicated directly with a reflux condenser, C, and a safety manometer tube, M_1, with a safety wash-bottle U containing a solution of boric anhydride in sulfuric acid, made up as described above; this was followed by a tube packed with alternate layers of glass wool and phosphorus pentoxide, and by a pair of condensing and distilling tubes, T_1 and T_2, each provided with a safety manometer tube M_2 and M_3.

The reaction mixture in flask A was heated on a steam bath for an hour, while the air was pumped out of the apparatus; during this time no noticeable gas evolution took place. Heated with a free flame, however, the reaction temperature was soon reached, and the positive heat of reaction was sufficient to maintain it. With the intervening stopcock open, and a bath of liquid air surrounding T_1, the gas condensed to a white solid, and melted to a clear limpid liquid. On some occasions, the liquid boron fluoride contained particles of a white solid floating around, which may have been hydrogen sulfide, as reported by Gray and Burt, or carbon dioxide, or a product of the interaction of boron fluoride with phosphorus pentoxide, a reaction that seems to take place with some readiness.

After collecting as much of the gas as was required, the reaction was interrupted by cooling flask A, and the condensed gas was subjected to a series of fractional distillations between T_1 and T_2, rejecting the first and last fractions in each distillation, and the purified product was finally stored in F, a 15 liter globe, previously evacuated and dried. When required for use, the gas was recondensed in T_2 with liquid air. During storage, some change occurred, evidenced by the fact that, on evaporation, a white deposit was left, which sublimed at a higher temperature; it is not clear what this was, though it may have been one of the fluorides of silicon, produced by the action of hydrogen fluoride on the glass[1]: the presence of hydrogen fluoride may be accounted for on the assumption of incomplete drying of the storage flask. A few additional fractional distillations sufficed to eliminate all traces of this impurity.

Preparation of Hydrogen Sulfide

Hydrogen sulfide was prepared by the action of constant-boiling hydrochloric acid (minimum vapor tension) on carefully washed zinc sulfide, freshly precipitated from a solution of zinc acetate: the reaction took place in a one liter flask, B, which contained the zinc sulfide; the acid was added as needed from the dropping funnel sealed into the neck of B. The evolved gas was freed from hydrogen chloride by bubbling it through a suspension of freshly precipitated aluminium hydroxide in water contained in the safety wash bottle W, and through the gas bubbler V, containing water, dried by contact with anhydrous calcium chloride and phosphorus pentoxide, and finally condensed in tube T_4 in a bath of carbon dioxide snow and acetone. The safety manometer, M_7, interposed between the reaction flask B and the wash bottle W, is essential, as any clogging of tubes in W or in the drying tubes might give rise to serious consequences.

Cardoso[2] has very ably discussed the impurities accompanying hydrogen sulfide, which is difficult to obtain perfectly pure, and has devised elaborate precautions for their elimination. For our purposes the product obtained after three fractional distillations was of sufficient purity, and was stored in the globe marked R until required, when it was condensed in T_3.

---

[1] See Germann and Booth: J. Phys. Chem. 21, 83 (1917).

[2] Gazz., 51 I, 153 (1921).

The Freezing Point Measurements

The central portion of the apparatus was devoted to the measurement of the gases, the preparation of the solutions, and to the measurement of the freezing points. The details are similar to those described by Baume[1]. The gases were measured volumetrically in the calibrated flasks H and G, packed in cracked ice to maintain constant temperature. The pressure of the gas was measured on the baro-manometer P, one side of which could be evacuated by opening the stopcocks 2 and 1 leading to the vacuum apparatus, thus making the readings independent of atmospheric pressure. To measure a quantity of boron fluoride, for example, stopcock 4 of flask H, and stopcock 3 leading to the manometer were opened, and boron trifluoride was allowed to evaporate through stopcock 5 into the evacuated space thus made available, until the pressure reached a little more than one atmosphere. 5 was closed, and the pressure read and recorded; 4 was then closed, and the dead space between it and the manometer evacuated by liquid air condensation of the gas it contained into T_2, by opening 5 for a few moments. H then contained a known volume of gas under a known pressure, P', at a known temperature, 0°. The dead space between the mercury of the pressure manometer and the stopcock of the measuring flask contained the same gas at a pressure P'', equal to its vapor tension at the temperature of the cooling bath used (liquid air or liquid nitrogen, sometimes liquid oxygen). The gas in H was then transferred to the freezing point tube L by liquid air condensation, opening 4 and 6 for the purpose; when no further condensation occurred, 6 was closed, and the pressure P'' was read on the manometer P; the weight W of the gas condensed in L was then (neglecting the small correction for the deviation of the gas from Boyle's law)

$$W = \frac{L\,V\,(P'-P'')}{1000 \times 760} = \frac{L\,V\,P^\circ}{1000 \times 760}$$

where L is the weight of the normal liter of the gas, V is the volume of the measuring flask in cc., and P° is the pressure. Since, however, the molecular composition of the solution was required, rather than the composition by weight, the mass of the gas used was not actually needed. Assuming the perfect gas law, we have

$$\frac{M_g}{M_h} = c\,\frac{P_g^\circ}{P_h^\circ}$$

where M_g and M_h are the number of moles of the two gases measured in G and in H, P_g° and P_h° the pressures of the two gases, and c the ratio of the volumes of the two flasks,

$$V_h = c\,V_g.$$

Correcting for the deviation of the two gases from the perfect gas laws, we have

---

[1] J. Chim. phys. **9**, 245, (1911); **12**, 206, 216, 225, 242, 250, 256, 270, 276 (1914).

$$\frac{M_g}{M_h} = c\,\frac{P_g^\circ + \frac{P_g^\circ}{760} A_g']_0^1}{P_h^\circ + \frac{P_h^\circ}{760} A_h']_0^1} = c\,\frac{P_g^\circ (760 + A_g']_0^1)}{P_h^\circ (760 + A_h']_0^1)}$$

where $A_g']_0^1$ and $A_h']_0^1$ are the compressibilities of the gases in G and H between zero and one atmosphere. The mole fraction Xg of the gas in G is given by

$$X_g = \frac{M_g}{M_h + M_g} = \frac{c\,P_g^\circ (760 + A_g']_0^1)}{P_h (760 + A_h']_0^1) + c\,P_g^\circ (760 + A_g']_0^1)}$$

The corrective factors are small and may be neglected in most cases, especially if the gases are in approximately corresponding states at 0° and one atmosphere. In this case the calculation takes the simple form

$$X_g = \frac{M_g}{M_h + M_g} = \frac{c\,P_g^\circ}{P_h^\circ + cP_g^\circ}$$

The volumes of the two globes were 893.53cc. for G, and 896.50cc. for H.

Enough gas was condensed in L to cover the bulb of the thermometer; then the freezing point was determined, using as cooling agent a bath of liquid air, separated from the freezing tube by an air jacket J, containing a few pieces of anhydrous calcium chloride to prevent the formation of hoar frost in the annular space between the jacket and the freezing tube. The liquefied gas was stirred by the vertical motion of a spiral glass stirrer S, actuated by the attraction of an electromagnet E for a soft iron collar K attached to the top of the stirrer; the electromagnet worked intermittently, having an electrically connected metronome in the circuit.

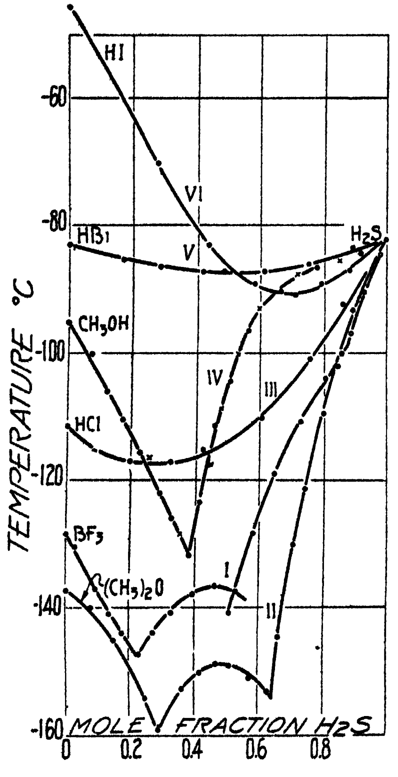


Fig. 2

A small amount of the second gas was then measured into the freezing point tube, and the freezing point observed again, and so on until the solution was approximately equimolar with respect to the two components. A similar routine, beginning with the second gas, and adding small amounts of the first, gave the data for the other half of the freezing point curve.

The thermometer employed was a liquid propane thermometer, constructed by Mr. Pierre E. Haynes, Director of the Linde Air Products Research Laboratory, of Buffalo, N. Y., and presented by him. The correction curve for the emergent column was prepared by observing the freezing points of a number of pure liquids, chosen so as to give points at intervals along the scale. The corrected temperatures are probably accurate to one or two degrees. However, for our purposes, relative rather than absolute temperatures were required, so that an error from this source would not impair the validity of conclusions bearing on the chemical affinities of the substances studied.

In Table I are the data with which the curve in Fig. 2 was constructed.

TABLE I

P°_g H_2S mm.	P°_h BF_3 mm.	Mol. Frac. H_2S	Average Temp. F. P. °C.	$P^\circ_g H_2S$ mm.	$P^\circ_h BF_3$ mm.	Mol. Frac. H_2S	Average Temp. F.P. °C
3170.0	0.0	1.000	− 82	108.6	2350.3	.044	−135
”	44.3	.987	− 84½	156.2	”	.063	−132
”	85.7	.974	− 86½	200.8	”	.079	−137
”	250.5	.927	− 90½	247.3	”	.095	−137
”	329.3	.907	− 93½	290.9	”	.110	−139
”	415.4	.884	− 97	332.6	”	.124	−139
”	518.1	.860	−100	370.3	”	.136	−141
”	639.3	.833	−102	421.0	”	.152	−143
”	780.1	.803	−104	501.3	”	.176	−144
”	976.4	.765	−106½	594.9	”	.202	−146
”	1170.7	.731	−111	689.2	”	.227	−147½
”	1361.8	.700	−113	781.6	”	.250	−146
”	1542.1	.674	−116	885.0	”	.274	−144
”	1761.4	.644	−119	1008.5	”	.301	−142
”	2025.2	.611	−125	762.3	1558.5	.329	−141
”	2291.9	.581	−128½	879.0	”	361	−139½
”	2540.3	.556	−133	1013.1	”	.395	−138
”	2808.4	.531	−137½	1173.8	”	.430	−137½
”	3059.7	.510	−141	1347.0	”	.464	−136
0.0	2350.3	.000	−128½	1524.9	”	.495	−137
39.1	”	.016	−131	1947.6	”	.556	−130
75.0	”	.031	−130½				

For purposes of comparison, the data relative to other systems containing hydrogen sulfide as one component have been plotted along with the curve for the system here studied. These include systems of hydrogen sulfide with hydrogen iodide and with hydrogen bromide, by Bagster[1]; hydrogen sulfide with hydrogen chloride, by Baume and Georgitses[2]; and hydrogen sulfide with methyl alcohol and with methyl ether by Baume and Perrot[3].

---

[1] J. Chem. Soc., **99**, 1218 (1911).

[2] J. Chim. phys., **12**, 250 (1914).

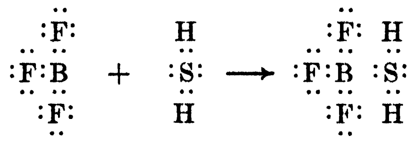
[3] J. Chim. phys., **12**, 225 (1914).

Discussion

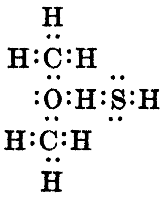
The system boron fluoride-hydrogen sulfide (see curve 1) presents a maximum at −137°, with a solution containing equimolecular quantities of the two gases, showing the existence of the compound $BF_3 . H_2S$. This compound is considerably dissociated at the melting point, as shown by the fact that addition of either of the products of dissociation to the compound has little effect on the freezing point[1], yielding a well rounded maximum. The curve shows two eutectics, one on either side of the maximum, one at −148° with 22% of hydrogen sulfide, the other at −140° approximately, with 53% of hydrogen sulfide.

The form of the curve at −99° with 87½% of hydrogen sulfide indicates that this is the transition point of a crystalline addition compound, whose formula seems to be $BF_3 . 7H_2S$, and which dissociates into boron fluoride and hydrogen sulfide at this temperature.

Comparing with the diagrams for the other systems that have been recorded in the literature, it appears that boron fluoride has more affinity for hydrogen sulfide than have any of the other substances. Methyl ether, which is noted for the readiness with which it yields oxonium compounds, yields a diagram that is almost identical with that for boron fluoride, except that there is no indication of a higher hydrosulfide. If we assume with Lewis[2] that boron fluoride possesses three electron pairs in the valence shell of boron, we can easily represent graphically the structure of the first compound as one in which a lone electron pair of hydrogen sulfide is attracted to the boron atom in such a way as to complete its octet:—



Boron fluoride is known to form compounds with the ethers[3], in which the union may be represented in the same way, oxygen occupying the place of sulfur, and methyl groups the places of the hydrogen atoms; but in the addition compound between methyl ether and hydrogen sulfide, the hydrogen bond[4] evidently serves as the linkage between oxygen and sulfur, since the octet of each is complete:



---

[1] Kremann: Monatshefte, **25**, 1215 (1904).

[2] "Valence and the Structure of Atoms and Molecules", p. 98 (1923).

[3] Gasselin: Ann. Chim. Phys., (7) **3**, 28, 48 (1894).

[4] Latimer and Rodebush: J. Am. Chem. Soc., **42**, 1431 (1920); Huggins: J. Phys. Chem., **26**, 614 (1922).

Judging from the form of the maxima, the sulfhydride of boron fluoride and that of methyl ether are dissociated at their respective melting points to about the same extent, indicating that the two types of linkages, that between sulfur and boron on the one hand, and that between sulfur and oxygen via hydrogen on the other, are about equally strong, neglecting the difference in the temperature.

Any attempt to account for the non-formation of molecular compounds between hydrogen sulfide and the hydrohalogens and methyl alcohol would require a comprehensive analysis of all the known addition compounds of these substances, as well as of other similar ones. For example, why should the mere replacement of a methyl group in methyl ether by a hydrogen atom render the attraction of the oxygen atom for hydrogen sulfide inoperative? Is the temperature at which the alcohol-hydrosulfide eutectic separates so high that the addition compound is completely dissociated? That halogen atoms may unite with sulfur by means of the hydrogen bond is evidenced by the compound $BF_3 . 7H_2S$; why do the halogen atoms in hydrogen chloride, hydrogen bromide and hydrogen iodide not yield addition compounds? It is true that Pollitzer[1] found the solubility of hydrogen sulfide in aqueous hydrogen iodide greater than in pure water (100% greater in 7N – HI, and 15% greater in 10 N – HCl), which has been interpreted as evidence of compound formation[2], but other evidence given by Pollitzer would seem to indicate that some other explanation would fit the facts better.

The experimental work described here was performed in 1920 at the Morley Chemical Laboratory of Western Reserve University. The liquid air used was supplied by the Linde Air Products Co., to whom we desire to express our appreciation.

Summary

The freezing point curve of the system boron trifluoride – hydrogen sulfide, has been investigated, and has been found to contain two eutectics, a maximum corresponding to $BF_3 . H_2S$, with freezing point –137°, and a transition point of a compound $BF_3 . 7H_2S$ at –99°.

Judging from the flatness of the curve at the maximum, the compound, $BF_3 . H_2S$, is considerably dissociated, so that there should be little difficulty separating H_2S as an impurity from BF_3 by fractional distillation.

Laboratory Products Company, Cleveland, Ohio,
and
Western Reserve University, Cleveland, Ohio.

---

[1] Z. anorg. Chem., **64**, 121 (1909).

[2] Lewis and Randall: "Thermodynamics", p. 106 (1923).

OLD AGE AND DEATH FROM A CHEMICAL POINT OF VIEW

BY N. R. DHAR

In two previous papers[1] we have discussed the question of ageing of sols and gels. As life processes are mainly due to catalysts and colloids, I shall endeavor to explain the phenomena of old age and of death, which have been described by Metchnikoff as the most mysterious of natural phenomena, from a purely chemical point of view.

When a lump of sugar is left in air at the ordinary temperature, no oxidation of the sugar takes place; but when the same lump is taken into the animal body it is burnt readily with evolution of carbon dioxide and water, supplying heat to the animal body. We now know definitely that the oxidation of sugar in the animal body is accelerated by the enzymes, which are always present in the animal system. The activity of these enzymes really controls the velocity of the oxidation of food materials in the animal body.

We have repeatedly observed that the chemical reactivity of a freshly precipitated substance is much greater than that of a substance prepared long ago. Thus when ferric hydroxide, chromic hydroxide, etc., are freshly precipitated, they dissolve very readily even in dilute HCl; whilst the same substances prepared in a similar manner and placed at the ordinary temperature in a flask even in contact with water lose much of their chemical reactivity and do not dissolve in dilute hydrochloric acid; even concentrated hydrochloric acid dissolves these old samples of hydroxides with difficulty. The adsorptive power of these substances decreases considerably on ageing. Moreover we have shown that the catalytic decomposition of hydrogen peroxide due to the presence of manganese dioxide is much greater when it is freshly precipitated than when the same weight of an old sample of manganese dioxide is used. The generation of oxygen is much greater in the same time with a fresh sample of manganese dioxide than with an old sample.

It is well known that the percentage of water which enters into the composition of the animal body decreases with the age of the animal in question as will be shown in the following lines:—

A three-months' human fetus contains 94 percent water; at birth the water content is from 69 to 66 percent; in adult life 58 percent. It is held that in old age, the water content decreases; turgescence in general, and of the skin in particular, is obviously lost. With ageing there occurs shrinking.

From our experience on gels and sols we know that ageing of a sol is always associated with its dehydration.

We shall now utilize these results in the explanation of old age and death from a purely chemical point of view. We have already mentioned that the speed of the oxidation of food materials is essentially dependent on the activity of the catalysts inside the animal body, provided a sufficient supply of food and air are available for the animal body. Now just as a freshly precipitated manganese dioxide is more reactive as a catalyst in the decomposition of H_2O_2, similarly enzymes or other catalysts in the body of a child or a young man are likely to be more reactive than the enzymes or catalysts in the system of an old man. Consequently the amount of oxidation per unit weight of the body of a young person should be much greater than that obtainable in the case of an old person. As the animal or the individual grows older and older the amount of oxidation per unit weight of its body grows less and less as the enzymes and the activators in its body become more and more aged and inactive. It is well known that a certain minimum quantity of heat is necessary for the maintenance of the body temperature of about 37.4°C. When the system can not generate this minimum quantity of heat it breaks down and death follows. As time goes on the activity of the enzymes and other catalysts in the body becomes less and less and after a time a certain stage arrives in which the catalyst is unable to accelerate the oxidation of food materials by oxygen of the air to such an extent that the minimum quantity of heat required for the maintenance of the body temperature is obtainable. At this stage death is likely to occur.

---

[1] Dhar: Zeit. Elektrochem. **31**, 266 (1925); J. Phys. Chem. **29**, 435 (1925).

It also follows from the general dynamical principle that the free energy of a system tends to decrease.

We have repeatedly observed that a freshly precipitated sample of $Fe(OH)_3$, $Cr(OH)_3$, hydrated manganese dioxide, etc., loses its chemical reactivity more readily when kept at a higher temperature even in contact with water than when kept at a low temperature in contact with water. We have observed that the amount of adsorption of arsenious acid by a definite weight of $Fe(OH)_3$ kept at a temperature of 50° even in contact with water is much less than the adsorption of the same substance by the same weight of $Fe(OH)_3$ kept in contact with water at 25°; in other words, the decrease in the chemical activity of these substances or of ageing of these substances is more marked and more rapid when the substances are kept at higher temperatures than when kept at ordinary temperature. It follows consequently that MnO_2 will lose its catalytic activity towards the decomposition of H_2O_2 more readily when freshly precipitated MnO_2 is kept at a higher temperature than when kept at ordinary temperature and this is corroborated by experiments. It seems probable therefore that the life period of the enzymes and other catalysts in the human or animal body should decrease more readily if the human being or the animal has to live at a higher temperature than his body temperature. It follows therefore that the fall in the velocity and amount of oxidation of food materials in the animal body will be more marked with time when the animal lives in a warmer climate than when the animal has to live in a colder climate, because the catalysts lose their activity more readily at higher temperatures than at lower temperatures, though the amount of oxidation in a warm country will be larger in the beginning than in a cooler country. Moreover as the catalyst has to oxidize a greater quantity of food material at a higher temperature in an unit of time, its activity should decrease more rapidly.

Consequently it appears that old age and death would take place more quickly in warmer climates than in colder climates, under otherwise identical conditions, especially with cold blooded animals. Krehl and Soetbeer[1] have compared the heat production of animals from temperate climates (Lacerta, Rana) with tropical forms (Alligator, Uromastix) and found higher figures for the former than for the latter at identical temperatures.

TABLE I

Heat Production of Different Animals

	Weight in Grms.	Cal. per Kg. and hour. at 25.3°	Cal. per Kg. and hour. at 37.°
Lacerta	110	0.8	1.5
Rana	600	0.5	0.95
Alligator	1380	0.3	0.47
Uromastix	1250	0.26	0.4

Statistics show that the average longevity of human beings in tropical countries is much less than the average longevity of human beings in colder countries, as in tropical countries for some time of the year, the outside temperature is higher than the body temperature.

There is some direct experimental evidence available on this question from the work of Loeb and Northrop[2], Table II.

TABLE II

Effect of Temperature on Duration of Life of Drosophila (fly)—a cold-blooded insect.

Temperature °C	Total Duration of Life from egg to death.
10	177.5 days
15	123.9 "
20	54.3 "
25	38.5 "
30	21.15 "

From this table it is seen that at the lowest temperature the duration of life is longest, and at the highest temperature shortest. Cold slows up the rate of living for the fly. Heat hastens it. One gathers from the account which Loeb and Northrop give of the work, that at low temperature the flies are sluggish and inactive and perhaps live a long time because they live slowly. At high temperatures, on the other hand, the fly is very active and lives its life through quickly at the pace that kills. This relation is more easily applicable to cold-blooded animals. In the case of warm-blooded animals the relation is more complicated because of the so-called chemical heat regulation, as will be shown in the subsequent paper.

---

[1] Pflüger's Archiv, **77**, 611 (1899).

[2] J. Biol. Chem., **32**, 103 (1917).

The activity of the catalysts or the body cells is usually associated with its surface energy. In course of time the surface energy of all systems tends to decrease. Consequently the activity of the cells or enzymes is likely to decrease because of the fall of their surface energy with time; hence their catalytic activity is likely to decrease with time. It is quite possible for the membranes or tissues in the body which consist mainly of cells or protoplasms become hardened in course of time due to their partial coagulation and dehydration. It should be emphasized that dehydration and decrease of surface energy play a very important rôle in the catalytic activity of tissues, membranes, enzymes, and cells.

There are several biological facts in support of the above views. In investigations made upon isolated organs, it has been shown that a certain minimum metabolism involving respiratory exchange is inseparable from the life of every organ and will persist when the organ is doing no work whatever so long as the ability to do work remains.

Comparative experiments on the standard metabolism at different ages have been made on man by Magnus-Levy and Falk (1899). The older experiments of Tigerstedt and Sondén (1895) were also made on man, but the standard conditions were not rigorously observed. The general results of Tigerstedt and Sondén's experiments were very similar to those of Magnus-Levy and Falk.

Calculated per unit weight (kilogram) the metabolism of growing individuals is much larger than of adults, and in old age there is a distinct decrease. Adult individuals belonging to the same species, but of different size, have a larger gas-exchange per kilogram, the smaller their size, while it has been shown that when the metabolism is calculated per unit surface (square metre) about the same figure is obtained for all sizes. A comparison between young and adult human beings must therefore be instituted on the basis of surface instead of weight, as there are large differences in size. When this is done, Magnus-Levy and Falk find that the differences, though of course diminished, are not abolished as Table III shows.

TABLE III

Standard Metabolism of Males of Different Age

Age, years.	Weight, Kg.	Surface Sq. M.	Per square metre and minute	
			Oxygen c.c.	CO_2 c.c.
2.5–11	11.5–26.5	0.627–1.094	175–154	501–122
10 –16	30.6–57.5	1.205–1.834	159–132	133–109
22 –56	43.2–88.3	1.516–2.441	129–111	105–82
64 –78	47.8–69.3	1.622–2.077	103–87	86–63

Magnus-Levy and Falk have also made experiments on three subjects of approximately the same weight and height (and consequently the same surface) but vary different age. They obtained the results given in Table IV;

TABLE IV

Standard Metabolism of Persons with Same Surface

Age, year's.	Weight, Kg.	O_2 per minute c.c.	O_2 per Kg. relative figures.
15	43·7	217	110
24	43·2	196	100
71	47·8	163	75

but individuals of the same age and stature may also have very different standard metabolisms. Consequently, these experimental results support the view that old age is associated with marked decrease of the catalytic activity of the body enzymes and consequently in old age there is a marked decrease of metabolism. Death, according to this point of view, follows when the amount of oxidation in the body is just less than the minimum necessary to keep up the body temperature.

Summary

1. The chemical reactivity and adsorptive power of freshly precipitated substances are greater than those of substances prepared long ago.
2. The catalytic decomposition of hydrogen peroxide due to the presence of manganese dioxide is much greater when it is freshly precipitated than when the same weight of an old sample of manganese dioxide is used.
3. Old age is associated with marked decrease in the catalytic activity of the body enzymes and consequently in old age there is a marked decrease of metabolism.
4. A certain minimum quantity of heat is necessary for the maintenance of the body temperature. When the amount of oxidation in the body is just less than the minimum necessary to keep up the body temperature, death is likely to follow.
5. Animal life is assumed to depend essentially on the catalytic activity of the enzymes in the animal body.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
June 9, 1925.

STRUCTURAL COLORS IN INSECTS. I

BY CLYDE W. MASON[1]

Introduction

On looking over the literature on insect colors, one finds a very striking lack of agreement on many points; the nature of various colors thought to be due to structural conditions has been the subject of a great many conflicting papers. The situation is hopeful, in that most people do not need to be convinced that structural colors are of widespread occurrence in the insect world, but in many instances there has been an unfortunate tendency to assume that all these colors are to be explained on the same basis.

Actually, to determine the relationship of the structural features to the color phenomena observed in any given case requires more than a cursory inspection, particularly since pigmental and structural colors are combined in many instances and mutually influence the appearance observed.

In a study[2] of structural colors in feathers the main criteria for the identification of different types of color were assembled, and their application to a number of typical cases was illustrated. The present paper is an attempt to carry out a similar study in the case of a sufficient variety of insect color types to show how such criteria may be applied to any given specimen. It is not the aim of the writer to present a mass of information regarding a large number of different insects, or to assume the position of referee in all disputed cases. Such material, where it does appear, is incidental to the main purpose of this investigation, namely the development of reliable and simple methods for distinguishing between pigment colors and the different types of structural colors, when present in insects, either singly or in combination. It is hoped that such methods may be applied by entomologists to any cases which are of particular interest. The speciments used in the present work (furnished through the kindness of Dr. W. T. M. Forbes, of the Entomological Department at Cornell) were chosen irrespective of genus or species, the aim being to secure as great a variety of types of color as possible—in other words, to "sample" the collection on the basis of color phenomena rather than entomological relationships, though, naturally, representatives of different orders are present in the assortment which was studied.

Such an effort is by no means original with the writer. Many other workers[3] have made extensive studies with more or less the same purpose in mind, but some of their findings are none too conclusive, and have placed emphasis on the specimen rather than the method, so a somewhat different line of attack is perhaps not out of order. Much that appears in the following pages is not new, but inasmuch as it either confirms or contradicts earlier observations, its inclusion seems justified, particularly since it must be taken into consideration in any conclusions which may be drawn.

---

[1] The investigation upon which this article was based was supported by a grant to Messrs. Bancroft, Chamot and Merritt from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Mason: J. Phys. Chem., **27**, 201, 401 (1923).

[3] Hagen: Proc. Am. Acad., **17**, (1881-82); Coste: Entomologist, **23**, **24**, (1890-91); Tower: Dec. Pub. Univ. Chicago, **10**, 33 (1903); Mallock: Proc. Roy. Soc., **85A**, 598 (1911); Biedermann: Handbuch vergl. Physiol., **3**, I, **2**, 1657 (1914); Onslow: Phil. Trans., **211B**, 1 (1921); Suffert: Z. Morphol. Okol. Tiere, **1** II, 172 (1924).

Distinction between Structural and Pigment Colors

To decide whether structure or pigment is the cause of a given color phenomenon, a number of tests are useful. Obviously, if some specialized structure functions in accordance with certain optical principles to produce color, the chemical nature of the tissue in which this structure is present will be of negligible importance, except in so far as it may render the physical structure susceptible to alteration by chemical reagents; but any treatment which alters the nature of the *optical system* will produce a modification of the color. On the other hand, if the color is due to selective absorption or reflection of certain of the constituents of white light by a pigment, it will be very little affected by alterations in its physical condition, but will be susceptible to any chemical treatment which alters its inherent nature.

In accordance with the above principles, a structural color should satisfy most of the following general criteria:

Hue altered by pressure, distortion, swelling or shrinking.

Color destroyed if system is made optically homogeneous by permeating with a liquid of the same index of refraction as that of the tissue, and color restored on removal of this liquid.

Color not destroyed by bleaching, or affected by chemical reagents unless these swell, shrink or destroy the tissue.

No pigment, except possibly black or brown, extractable by solvents or revealed by chemical tests.

All constituents of the incident white light accounted for, either in the reflected, transmitted, or scattered light.

Similar color phenomena duplicable with colorless substances in similar physical condition.

Iridescence of some sort generally exhibited.

The converse of the above will serve to characterize pigment colors, and usually the distinction can be made even more positive by further tests regarding the particular sort of pigment or structure concerned. Structural conditions may modify the appearance of pigmented tissues, while the lustre of the surface, or the presence of over- or under-lying colored tissues may also have considerable influence; a given pigment may exhibit different tints or shades, or even apparently slightly different hues, depending on whether it is present in a fine or course state of subdivision, or in combination with white. In most cases, even where the type of color is established, study under a Greenough-type binocular microscope at moderate magnifications will show the relative importance of these different factors in a most striking manner.

For instance, there is probably about the same amount of pigmentation in all the black beetles, but those which have highly lustrous surfaces appear much blacker than those which have their integument dulled and roughened by age and exposure. Supplying the "glaze" by means of a film of oil or varnish gives a deep lustrous black in such cases. However, even such glossy black is not as dark as the black of certain butterflies. These latter do not even show "highlights", yet their pigment is probably no more dense than that of the beetles. Their dark scales, naturally of little lustre and with numerous interstices between them, serve to "entrap" the light, and give a much darker shade for a given amount of pigment (just as velvet appears darker than satin dyed with the same dye). This appearance is particularly marked if one views the butterfly's wing from the tip, that is, looking down into the shadows between the scales.

It is highly probable that the browns and blacks are due to a melanin pigment, as they are in birds and mammals, the color present depending not only on the amount of pigment present but also upon its condition, black being found with granular pigmentation and brown with more or less perfectly diffuse pigmentation (pigment in solution rather than suspension in the tissue).

By permeating the tissue with a colorless liquid of nearly the same index of refraction (say 1.55-1.6 for chitinous material) the effect of any structures associated with the pigment to be studied is minimized, and the true absorption color may be observed by transmitted light.

Besides the ordinary colors which depend upon absorption of light, certain others have been ascribed to pigments: white, which depends on the power of scattering light, and certain cases of iridescent colorings, which are said to be due to pigments showing selective reflection. The latter will be considered in connection with the discussion of other iridescent colors with which they are most likely to be confused.

White in Insects

White depends for its perception on a rather high intensity of reflected or refracted colorless light reaching the eye of the observer without the perception of transparency or vitreous or metallic lustre. This will be the case whenever the surface by which such light is reflected or refracted to the eye are so small as not to be readily resolved as separate by the means of observation employed. Obviously, the finer the surfaces, the more perfect the "scattering" of light and the whiter the object. White objects, because of their power to scatter light in all directions, transmit light very imperfectly, and are more or less opaque, even though the actual material composing them is transparent (e.g.: snow and ice; foam or fog and water; sand and rock crystal; blanc fixe and barite; chalk and Iceland spar; "Rayon" and "Cellophane", and so on). The colorless metals appear white by reflection from irregular surfaces but in the case of all other colorless substances, refraction also plays a part in scattering the light to produce white, and the elimination of the reflection and refraction at their numerous small bounding surfaces results in transparency, with no whiteness. Since this reflection and refraction by transparent materials depend upon the relative indices of refraction of the substance and the medium surrounding it, it is obvious that if the latter can be varied, (as it can in two-phase systems when at least one phase is fluid) the white may be completely destroyed, by rendering the system *optically homogeneous*. So whenever we have practically colorless chitin in such form as to present many more or less unordered reflecting surfaces, we shall observe whiteness. Nearly all of the whites of insects are to be explained on this basis, as proved by the fact that when the air in contact with the chitin is replaced by a liquid of index of refraction near 1.55 they are rendered colorless and transparent, while if the liquid is either of greater or less index of refraction the destruction of the white is not so complete. On removal of the permeating liquid, the original whiteness is restored, proving that no white "pigment" has been dissolved out.

The above procedure may readily be followed under the microscope, and the connection between air as a permeating medium, and the whiteness is very evident by reflected light or dark field illumination. The increase in transparency as the liquid penetrates the interstices of the structure is very striking, and corresponds to the familiar process of "clearing" tissue for microscopic study. By means of the "Becke test" (given in any text-book of petrography) one can select from a series of liquids one which matches the index of refraction of the chitin almost perfectly, and thus render it almost completely invisible, even by dark field illumination. The scales of white butterflies and moths illustrate this very nicely.

The question as to whether the whites of insects are due to pigment or to structure is merely one of definition. All white materials, whether commonly thought of as pigments or not, owe their whiteness to the reasons given above, and white paint is just as much a structural white as snow. We are ordinarily in the habit of thinking of pigments as something distinct from the substance which is pigmented by them, and from this point of view there are very few white pigments in nature. Generally the tissue in question is its own white pigment, and the white cannot be removed without destroying the structure on which it depends.

Certain butterflies, notably the *Pieridae* are said to owe their whiteness to a definite pigment (uric acid) which is present in their scales as an excretion from one stage of their development.[1] Although uric acid is white, and might well serve as a pigment when finely divided, it plays a very minor part in producing the white of butterfly scales, for these may be extracted with solvents for uric acid (such as dilute alkalies) but on washing and drying their white appears undiminished. The scales become transparent on penetration with liquids of $n = 1.55$-1.6. Assuming that any uric acid is present in the free state, and not in solid solution in the chitin, it might be expected to appear white when finely divided, but the ribbed and reticulated structure of the scales accomplishes this so well that whether uric acid is present or not is of little importance, as far as their whiteness is concerned.

---

[1] Hopkins: Phil. Trans., **186**, 661 (1896).

The belief that the chalky whites of butterflies, particularly the Pieridae, are due to pigment is common; but the more lustrous whites, such as those of *Euproctis* are ordinarily admitted to be air-filled cavities in the scales. Actually both sorts have hollow scales, as do insects in general; both are rendered transparent by permeation with liquids of n = 1.55-1.6., and there is no question but that, whatever may be the chemical composition of the scale in both cases, the white is due to essentially the same causes, namely, the scattering of light by reflection and refraction by the minute structures of the scales.

Lustrous Whites

The question of lustre is closely related to that of color, and may best be discussed in connection with white, for we have all types illustrated by colorless insects. White butterfly wings exhibit lustres ranging from chalky to micaceous, silvery, or pearly, and these are of necessity to be explained on the basis of the structures present, since the constituents of the wings are essentially the same in all these cases.

Chalky or matte lustre is characterized by the absence of high lights, and by practically uniform scattering of light in all directions. This requires a random arrangement of the surfaces which reflect and refract the light. Although the scales of butterflies are arranged systematically on the wing membrane like shingles on a roof, this is not of importance in the case of the chalky whites, for the individual scales serve to scatter light in all directions, whatever their arrangement may be; a single scale appears just as white as do a group of scales. The overlapping of the scales on the wing contributes little to their whiteness, because of the high degree of opacity of the white. Such scales, under the microscope, show more or less regular longitudinal striations, boldly defined, and probably due to deep corrugations in the surface of the scale, or to longitudinal partitions in it, or to both. Besides these, fine transverse markings are present, which, although unordered in their pattern, add materially to the opacity and whiteness. On permeating with a liquid of n = 1.55-1.6 the markings and outline of the scale become almost invisible. The above multiplicity of fine structural details furnishes reflecting and refracting surfaces to scatter the maximum amount of light in all directions, and to give the minimum of sheen.

Intermediate between the matte whites and the pearly or silvery whites is that shown by *Euproctis*. Here a distinct sheen is observable, when the line of vision is that direction along which light would be reflected by the surfaces of the scales. In other positions the wing appears matte white, tho not so bright or opaque as in the case of the typical chalky whites; single scales appear very much more transparent and scatter less light than when grouped on the wing, where under the Greenough they are seen to overlap considerably; this overlapping adds to their reflecting power, for if a blackened scalpel is inserted under the free edge of the scales they permit it to be seen thru them very clearly. With high powers, the individual scales are seen to be striated longitudinally, but these markings are very much less distinct than in the scales of the *Pieridae*, and constitute the only surfaces for scattering light, the finer reticulations being absent. The whole appearance is that of considerable transparency, even without a permeating liquid; when the scales are filled with liquid of $n = 1.55\text{-}1.6$ they are barely visible under the microscope, and the entire wing is rendered so transparent that one may easily read thru it, even when the liquid chosen does not match the index of refraction of the scales very perfectly. In the above case, the white is due to a certain amount of scattering by the finer structures of the scales but we have here also the necessary structure for the production of pearly lustre, namely, the superposed transparent reflecting surfaces presented by the scales as they lie on the wing. This is the situation which is present in all cases of pearly lustre, such as mother-of-pearl, ground mica, crystallized CdI_2, or a pile of glass plates[1], and it is of considerable importance also in the production of metallic lustre[2].

The essential difference between matte whites and pearly whites depends on the amount of random scattering which the presence of minute structures in the scales may cause.

When the lamellae which produce pearly lustre are almost perfectly plane and transparent, and there is a minimum of diffuse scattering of the light, we have very perfect and typical pearly lustre, which may under favorable circumstances verge into true metallic lustre. This is exhibited by *Helicopus cupido* and by the common "Silverspot" (*Argynnis*). The name of the latter is very appropriate, for the spots, though not as metallic as burnished silver, strikingly resemble matte silver. They do not scatter light well, and only along the line of direct reflection do they appear bright. Even in this position they do not send as much light to the eye as do the chalky white scales. Microscopic study of the scales shows longitudinal striations and a distinctly transparent appearance. There is some scattering of the light which falls across the striations, but on the whole a rather glassy appearance is noted by reflected light.

The pearly areas of *Helicopis cupido* are similar in appearance to those of the "Silverspot", but are even more highly lustrous and show distinct though pale iridescent colorings, which strongly resemble those of mother-of-pearl. The overlapping, transparency, and lack of light-scattering power or whiteness are even more pronounced; microscopically the scales show only very faint striations and appear to be little more than a transparent envelope with thin walls nearly in contact, all of which constitutes a system for the production of pearly or metallic lustre by superposed laminae, more perfect than that of *Euproctis* because of the almost complete transparency and absence of diffusion of the light. However, even here the whiteness and reflecting power at the most favorable angle are rather less than in the matte whites.

Leydig[3] has ascribed the pearly lustre of *Argynnis* to the fine structure of the scales, without specifying how this is related to the general phenomenon of pearliness, and Biedermann[1] while disagreeing with him on details, apparently also failed to recognize that superposed, more or less transparent lamellae were in themselves sufficient to account for all the observed lustre. Süffert[2] also places undue emphasis on the minute structural details of the scales, and considers their high reflecting power to be due to the longitudinal ridges of the upper lamella, which serve by two refractions and one total reflection to send the light back along the original direction, in somewhat the same manner as does ribbed glass. He admits that such a structure must be highly perfect if it is to function as indicated, but apparently does not appreciate the possibility of the high lustre being accounted for by any less complex system.

---

[1] Bancroft and Allen: J. Phys. Chem., **28**, 546 (1924); **29**, 564 (1925).

[2] "Silver" patterns on the wall paper are made with ground mica; a roll of waxed paper is pearly, while a roll of colorless, transparent "cellophane" (sheet viscose) is hardly to be distinguished from a polished steel rod.

[3] Arch. Mikr. Anat., **12**, 536 (1876).

Microscopic study of scales of *Argynnis*, with transmitted and with vertical illumination reveals a structure that is closely similar to that described by Süffert: a ribbed upper lamella, a fairly smooth lower lamella, an interior space with fairly plane surfaces and a relatively small amount of spongy or columnar material in this cavity. Slow permeation by viscous liquids aids in the interpretation of these appearances, and helps to isolate their several effects; for instance, the iridescent colors seen by axial reflected light are observed only when the interior of the scale is empty, irrespective of whether the lamellae are in contact with liquid outside. The dry scale is apparently the same viewed either side up. If the scales are covered by a cover glass, and a viscous liquid is allowed to surround them, one notices that the reflecting power of unwetted scales is apparently no greater than that of the air spaces between the slide and the cover glass. Also, if one compares the reflecting power of the scales on the wing with that of a single thin film of glass, the latter is much more brilliant, yet when we consider that the scales consist of two lamellae, separated by an air space, and that they overlap so that they are two deep on the wing, it is evident that we might expect an even higher degree of reflection from the four films of chitin thus functioning as reflectors.

Actually it appears that the high lustre of the pearly scales is *in spite of* rather than because of their fine structure. The latter plays its part in diffusing the light, so that the metallic appearance is visible over a wider angle, and in producing certain color phenomena, but acts to cut down the efficiency of the multiple-film system for producing metallic or pearly lustre; this loss in specularity of reflection is accompanied by an increased appearance of whiteness, and greater opacity of the scales.

The delicate iridescent colorings, the cause of which will be discussed later, enhance the resemblance to pearl, and possibly give the illusion of even greater lustre.

Non-Porous Whites

In addition to the ordinary sort of structural whites in which the minute surfaces are in contact with air, another type may occur in which the structure is non-porous, and possesses no air-filled spaces. The reflection and refraction which are the cause of the scattering of the light take place at surfaces bounding two tissue materials of different refractive indices, and their perfection will be governed by the amount of this difference. Such a system is optically the same as a porous white rendered partially transparent by a liquid of index of refraction fairly near that of the tissue but not matching it; examples are common: marble, vitrified porcelain, ivory, pearl, paraffin wax, etc.

---

[1] Handbuch vergl. Physiol., 3, I, 2, 1932 (1914).

[2] loc. cit. p. 287. Z. Morphol. Okol. Tiere, 1 II, 172 (1924).

Obviously, any attempt to destroy the white by rendering it transparent by means of a permeating liquid cannot be successful, for there are no interstices to be filled. The only possibility would be in some way to render the indices of refraction of the various structures identical, which would involve chemical alteration, hydration or some similar treatment.

The non-porous whites are of very little importance in the insect world, and are mentioned merely for the sake of completeness; the "air whites" may definitely be said to be the only important cause of whiteness in insects. In most cases whites of this sort are more or less transparent, and of little scattering power; in insects this is particularly true, because the various kinds of material which make up the tissues have almost the same index of refraction; in no case is the difference in the indices nearly as great as the difference between one of them and that of air. Wing membranes, when bare of scales, and occasionally veins may give a weak white, but these play a very small part in the whiteness of the insect as a whole.

Influence of Structure on Coloration

Where a color pigment is combined with white it is usually dissolved or dispersed in the tissue itself, so that we have to deal with a more or less colored and transparent substance, which is in a state of subdivision corresponding to that existing in the whites. Unless the tissue is very heavily pigmented and rendered almost opaque, such fine structure will reflect a large part of the incident light; what light does actually enter the colored tissue will be refracted and reflected out again, without traversing more than a very short distance in the tissue. Thus there will be little absorption, although the scattering of the light takes place just as in the unpigmented tissues and as a result we have the hue of the pigment with a large admixture of white, giving a tint much lighter than the tissues would exhibit if the fine structure were absent. Many common materials illustrate this great difference in tint dependent upon their fineness; beer and its foam, vulcanized rubber and its dust, the "streak" of colored minerals, taffy before and after pulling, butter and cream, coarse and fine copper sulphate, and so on. It follows that, since structural conditions cause a very much lighter tint than shown by the colored substance in mass, the best way to observe the true hue and tint is by eliminating reflection and refraction as completely as possible. This is accomplished by rendering the system *optically homogeneous* by bringing a liquid of the proper index of refraction in contact with all the minute surfaces, just as is done when whites are rendered transparent.

The above treatment is particularly useful in studying the hue, concentration, uniformity, and state of aggregation of pigments in the scales of butterflies and moths, and one may rest assured that any color observed by transmitted light under these circumstances is due to pigmentation and not to any structural effect.

To the naked eye, permeation with liquids darkens the tint considerably and increases the transparency of the scales and of the wing as a whole. This behavior has many familiar analogues; wet and dry watercolors, grease or water spots on wood, colored fabrics, and papers, etc., mud and dust; copper sulphate may be powdered so fine as to be almost white, but its deep blue is restored by wetting with a liquid of the proper index of refraction.

Where pigmentation is combined with some specialized structure other than that capable of producing ordinary white, a number of effects are possible. Hairs and scales play a considerable part in modifying the tint and lustre of the pigment. The deep blacks and browns of some of the bees are closely analogous to the rich shades of velvet or plush; the hairs standing on end have their surfaces in position to reflect a minimum of light, and if they are even moderately pigmented appear in a very much darker shade than if they are lying more or less flat, (as in crushed velvet).

If the scales are all practically in the same plane, they present an excellent reflecting surface to light which falls along their length; this corresponds to the structure of satin, and, like it, may exhibit a very high lustre.

Ornithoptera poseidon exhibits two types of black which illustrate the influence of structure on pigment coloration. The deep velvety black which occupies most of the non-iridescent portion of the wing is due to the heavily pigmented, overlapping, convex scales, of low reflecting power, and with only a small portion of their curved surfaces in position to reflect light at any given angle. The brownish black areas just in front of the rear iridescent border of the upper sides of the forewings are markedly different in appearance; the scales are very much narrower and more numerous, stand erect, are sharply curved at the upper end and less heavily pigmented. They overlap very little, and permit the light colored wing membrane to be seen between them; under the microscope the appearance resembles that of open-weave Brussels carpet. Individually they show more reflecting power than do the scales from the deep black portions, and on the wing this is more pronounced because of the greater number of minute surfaces presented by the finer scales, and because of the partial visibility of the wing membrane between them.

It has been pointed out that relatively transparent, smooth, overlapping scales may show a pearly to metallic sheen; if these are colored this effect is greatly enhanced, and may be of typical metallic lustre[1]. The wings of *Chrysophanus virgaureae* and their members of this family have the appearance of tarnished brass, but their scales are as described above, with the addition of a yellow orange pigment. Dyeing the silvery scales of *Helicopus cupido* or

---

[1] A pile of three to five sheets of yellow gelatine has a metallic lustre equal to that of polished brass, and corresponding appearances may be obtained with other colors. Crystallized lead oxide looks golden; anhydrous chromium sesquichloride is a metallic purple; ground phlogopite resembles bronze; the goldfish is golden rather than yellow because of his scales.

Argynnis or the pearly ones of *Euproctis* with dilute Bismarck brown gives them a golden appearance. This metallic appearance of relatively smooth, transparent scales is observed irrespective of whether their color is due to pigment or to structure, and *Urania, Morpho, Apatura,* in fact most of the brilliantly lustrous and iridescent butterflies may be cited as examples, without discussing the nature of their coloring at present[1].

Biedermann[2] has discussed in considerable detail the relationship of the form and surface of insect scales to the color phenomena which they exhibit collectively on the wing of the insect. Convex, concave, warped, or stepped surfaces, or unusual inclinations of the scales may prevent their color (pigment or structural) from being seen except in certain directions.

The blue-green bars on the upper surface of the wings of *Apatura* (*Chlorippe*) *seraphina* are composed of scales which are strongly convex and form minute cylindrical surfaces, the axes of which are cross-wise of the scales. Some part of such surfaces is in position specularly to reflect light to the eye of the observer almost irrespective of the position of the wing as a whole, and the color bands may be seen from any position. The remainder of the upper surface of the wing appears dull brown, except in certain positions, where it is purple to blue-green, so that as the wing is inclined this brilliant color flashes out, only to disappear as suddenly with further inclination of the wing. Study with the Greenough-type binocular microscope permits this behavior to be observed at moderate magnifications with highly realistic stereoscopic effect, so that interpretation of appearances is greatly simplified. It is found that the scales in these brown to blue areas are not particularly convex but are markedly inclined to the surface of the wing, so that the tip is considerably higher than the base, and the plane of the scale makes an angle of about 30° with the plane of the wing. The reflection from these scales is specular, and as a consequence they appear bright only when the angle of incidence of the illuminating beam and the angle of reflection along the line of vision are equal[3]. These two factors combine to render the reflection color visible when one looks "along the grain" of the wing, while if the line of vision falls "against the grain" there is no reflection, and the effect is that of the brown pigmentation, the shade of which is darker because the scales are seen endwise and the interstices beneath them serve to "entrap" the light. All this may be checked varying the plane of the scales ("ruffling them up" or flattening them down) with respect to the plane of the wing, and study of single scales is also of value.

Essentially the same situation exists in *Apatura ilia,* and it is of interest to note that even the scales in the white bands possess the same blue reflections, which may be enhanced by dyeing them with a brown or black dye so that the white is eliminated. *Ancyluris meliboeus*, *Acraea sp.*, *Callicore eluina*, *Zephyrus quercus*, and numerous other butterflies show a bluish over-sheen or "bloom", in addition to their ordinary pigment coloring (commonly melanin brown).

---

[1] In discussing the influence of the form of the scales on the color exhibited by them, Onslow mentions the importance of flat, smooth surfaces in the production of metallic appearances. Phil. Trans., 211B, 5 (1921).

[2] Handbuch vergl. Physiol., 3, I, 2, 1657 (1914).

[3] It should be remembered that if the plane of the scale makes an angle of 30° with that of the wing, a vertical illuminating beam will be reflected at an angle of 2 × 30° from the normal to the surface of the wing. (A change of *n* degrees in the plane of the reflector causes a change of 2*n* degrees in the direction of the reflected ray.)

Tyndall Blues in Insects

The ability of a finely divided transparent substance to scatter light increases with increasing fineness until the order of magnitude of the particles is near the wave-length of light; for finer material the action is selective, and the particles scatter the short wave-lengths of white light, while permitting the longer wave-lengths to pass through unaffected. Such a system appears turbid blue to white from positions out of the line of the directly transmitted light and turbid yellow to red in this latter direction. Tyndall[1] first explained this phenomenon, and it has been recognized in a great number of common objects; the sky, blue eyes, smoke, "opal" glass, skimmed milk, blue feathers, very fine precipitates, collodion jelly, sublimates on charcoal in blowpipe analysis, etc.

The properties of Tyndall blues have been discussed at some length in a previous paper[2], and only the main criteria for their recognition need be summarized here: 1—Minute structure, of dimensions less than 0.5μ, of different index of refraction from that of the surrounding medium. 2—Blue to bluish white scattered; brown to red, orange, oı yellow by transmitted light. 3—Scattered light more or less polarized; vibrations in a plane perpendicular to the direction of the incident beam.

To observe the scattered light, it is desirable that the illuminating beam should fall more or less tangentially on the tissue under examination, and if any surface irregularities are present, the scattering of light by these should be eliminated as completely as possible, preferably by immersion in a liquid of the same index of refraction as that of the tissue. Dark field illumination is very satisfactory for the examination of Tyndall blues, but the polarization is not readily observed unless the light is unidirectional. A cap nicol prism above the eyepiece, with or without a "Selenite plate" serves to determine the polarization of the scattered light. By transmitted light with critical illumination and an objective of at least N.A. = 0.85 a thin layer of the material should show fine stippling, the individual particles being about 0.3μ to 0.5μ between centers. These may also be observed by reflected light under favorable circumstances. The color of the tissue is, of course, yellow to orange or brown, by transmitted light, unless dark pigment underlies the blue structure, and this may readily be noted. A dark background for the blue cuts off any stray light from below, so that only the scattered light is observed.

Biedermann[3] mentions Schatz as having ascribed the metallic blue of the *Morphos* to a turbid layer over a dark background and points out that the lustre and brilliancy of the color are inconsistent with the thickness of the structure where they are assumed to originate, while the change of hue with changing angle of incidence is certainly different from the behavior of Tyndall blues. Needless to say, no evidence structural or optical, has been found to support Schatz's supposition with respect to the metallic blues.

---

[1] Phil. Mag., (4), **37**, 385 (1869).

[2] Mason: J. Phys. Chem., **27**, 215 (1923).

[3] Handbuch vergl. Physiol., **3**, I, **2**, 1970 (1914).

In *Enallagmae* the blue of the abdomen lies over a dark layer, to which it is closely adherent, but it is possible to dissect away the underlying pigmented tissue, and to study the blue layer by itself. The criteria given above are all satisfied, although the polarization is not very distinct. In all probability this case of Tyndall blue is due to fine particles enclosed in a chitinous material, for the color is not destroyed by prolonged soaking in permeating liquids, and pressure has little effect on the blue, tho if pores were present they should be partially closed by this treatment.

Mesothemis simplicicollis is typical of dragon flies which develop a "bloom" with maturity; the color of the body of this insect is really only a very grayish blue, but it constitutes an example of Tyndall blue where air is in contact with the surfaces which scatter the light.

This "bloom" or efflorescence may be removed by scraping, leaving exposed the black or brown integument which serves as a dark background for the blue. The scrapings are in such a fine state of subdivision that they appear almost opaque by transmitted light and scatter light very effectively. However, their microscopic structure is indefinite and too coarse to give better than a grayish blue.

When the "bloom" is wetted by a liquid of index of refraction near 1.5 it becomes completely transparent and invisible and the dark pigmented tissue beneath it is perfectly visible. On removal of the liquid the original appearance is restored.

A somewhat similar "bloom" is found on the wings of *Libellula pulchella* ("Ten Spot"), in the form of white cloudy spots, which shade to whitish blue at their edges. This is a Tyndall blue, the white portion of the spot being due to a coarsening of the structure. Microscopic examination shows the spots to consist of a very fine granular coating on the wing membrane; this may be scraped off readily, and is rendered completely invisible by wetting with liquids of $n = 1.5$. Removal of the liquid restores the original appearance.

It is noteworthy that while all non-metallic blues in feathers are Tyndall blues, in insects examples are few, and most blues are due to other causes.

Of the possible specimens suggested by Dr. Forbes, only one was found to possess a blue pigment: the hairs of *Xylocopa Caerulea* are a clear blue by transmitted light, and show no evidence, structural or optical, of any but pigment coloration. The color change brought about by treatment with acids is undoubtedly of the nature of an indicator effect, more or less perfectly reversible by alkalies.

The conclusions of this paper are as follows:

1. All whites of insects are structural.

2. Pearly and metallic lustre are due to superposed transparent parallel laminae.

3. Tyndall blue occurs in a few insects.

4. Blue pigments do not appear to be present in insects.

5. Structural conditions may modify the appearance of pigment colors very markedly.

Laboratory of Chemical Microscopy
Cornell University.

THE ELECTROLYSIS OF ACID SOLUTIONS OF COPPER SULPHATE. II. CONSTANT CURRENTS

BY J. T. BURT-GERRANS

The experimental work of Mr. L. V. Redman[1] having shewn general agreement between certain predictions of the mathematical theory[2] of changes of concentration at the electrode, and the behavior of acid solutions of copper sulphate on electrolysis, it remained to enquire whether the want of sharper agreement was due to inaccuracy in the fundamental assumption of the theory (viz: that the diffusion constant of copper is independent of its concentration in the electrolyte employed) or was due to insufficient approximation in the laboratory to the ideal experimental conditions postulated by the equations. The present paper gives an account of experiments on the electrolysis at 18.0°C of acid solutions of copper sulphate with constant current, which were undertaken to answer this question.

I. THE ELECTROLYTIC CELL

Exclusion of air:—Mr. Redman himself had discovered one source of error in the apparatus used by him, viz: the action of air-saturated electrolyte on the copper electrodes. I therefore carried out all electrolyses in an atmosphere of carbon dioxide, after first freeing the electrolyte from air by evacuation. A large quantity of stock solution, containing 15.45 g. of copper per litre, was prepared by dissolving recrystallized (hydrated) copper sulphate in maximum-conducting sulphuric acid (30.5% acid by weight, about 7.6 normal); this was diluted with the same acid to the desired concentration before each experiment, and freed from air by evacuation in a thick-walled glass bottle standing in the thermostat. Carbon dioxide was then bubbled in for two minutes, the solution evacuated again, treated with the gas for two minutes as before, evacuated once more, then left for at least two hours in the thermostat in a slow current of the gas, which was obtained from a cylinder, and was washed with water and passed through sulphuric acid on its way to the electrolyte.

A few minutes before the electrolysis the electrolyte was transferred (by gravity, through rubber tubing) into the electrolytic cell (which had been standing ready for at least half an hour in the thermostat) and was protected again by the gas; two portions of 100 cc. each were removed at this stage for analysis, and two more after the electrolyses were completed, unless the four analyses agreed the experiment was rejected. The copper was determined electrolytically in a King's electrolytic outfit[3]; the solutions were almost neutralized with ammonia, and sodium nitrate was added to secure a good deposit.

---

[1] L. V. Redman: J. Phys. Chem., **29**, 1548 (1925).

[2] T. R. Rosebrugh and W. Lash Miller: J. Phys. Chem., **14**, 816-884 (1910). Equations from this paper are indicated by "R & M".

[3] Chem. and Met. Eng., **21**, 25 (1919).

Precautions to secure uniform thickness of film:—In his apparatus Mr. Redman secured a uniform electrolytic field by the use of two stationary non-conducting horizontal plates, one at the top and the other at the bottom of the (perpendicular) rotating cathode. It seemed quite possible that the friction of the electrolyte against these plates might affect the thickness of the "diffusion film" of liquid adhering to the cathode, by making it thinner near the ends of the cathode than near the middle; while the equations of the "mathematical theory" are based on the assumption that the film is of equal thickness throughout. I therefore reconstructed the cell, and provided three cathodes on the same shaft, (Fig. 1), separated from each other only by thin discs of insulating material ("Redmanol"); the three cathodes were of the same diameter (4.60 cm) and height (6.40 cm), and each was provided with its own rheostat so that the same number of amperes could be sent through each, but only the central cathode was connected to the oscillograph. The "current" recorded in the tables is that through the central cathode, and reached it by a mercury cup on the top of the shaft; the currents for the other two were led

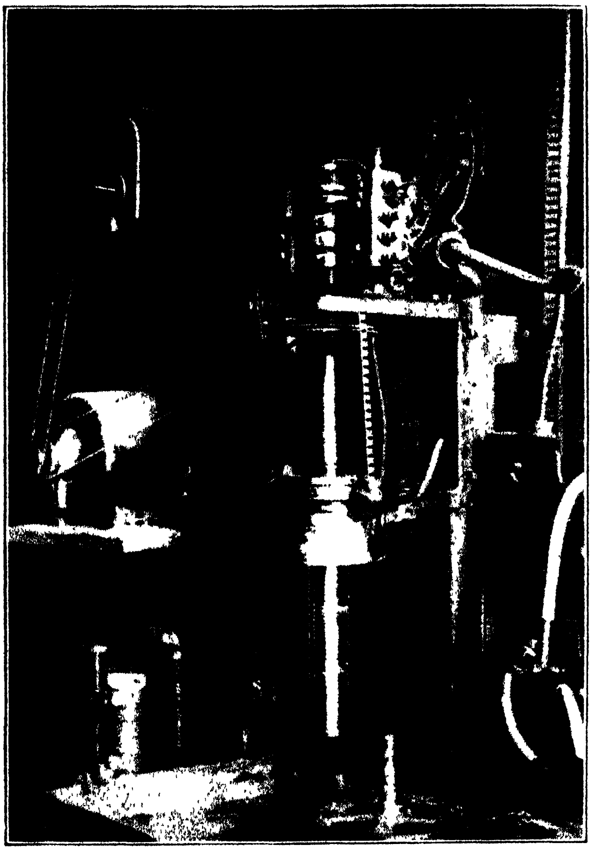


Fig. 1

in through brushes. The cathode shaft runs on a double-faced cone-bearing just above the cathodes and on a ball-bearing below the brushes. The common anode, which also serves as cell, is a drawn copper cylinder 10.2 cm internal diameter and 21 cm high, which screws into a flange on the casing of the lower bearing of the cathode shaft; it is provided with a delivery tube for filling the cell and with an overflow pipe to ensure that the electrolyte is always at the same level. The whole is mounted on a lathe bed set vertically, so that it can be lowered into the bath, whose temperature is held within 0.1°C by an electrically controlled thermostat.

Stationary horizontal insulating plates were employed, as in Redman's apparatus, one close to the top of the upper cathode and one close to the bottom of the lower cathode; with this arrangement the uniform electrolytic field was retained, but the plates were at such a distance from the central cathode that there seemed little danger of their affecting the thickness of its adherent film.

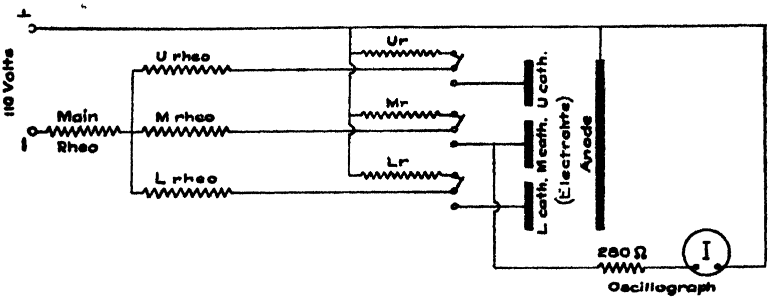


FIG. 2

II. THE CIRCUITS

Rearrangement of circuits. Redman's tuning-fork method of calibrating the time axis on the film, and of recording the rate of rotation of the cathode shaft, was retained; but the short-circuiting bar used to protect the cell while the current was being adjusted was found to leak a little, and was replaced by an automatic device which threw the cell completely out of circuit and replaced it by an equivalent resistance, except while the oscillograph shutter was open and the record was actually being made.

Three exposures were needed for each film, one to record the line of zero voltage, one for the voltage-calibration line, and one for the voltage-time curve taken during the electrolysis. For each of these special electrical connections were required, which were made by amalgamated copper contacts mounted on wooden blocks and dipping in the cups of a 48-cup mercury switchboard. The actual electrolytic circuit was kept away from this board for fear of accidental leaks; therefore, before each exposure a number of well insulated knife-switches had to be opened or closed by hand, but for each operation the mercury switchboard kept a red light burning near each switch, and this was extinguished only when the switch was moved to the proper position for the operation in hand. This arrangement much facilitated the manipulation of what, in the end, became a very complicated piece of apparatus.

Without going into details of the mercury switchboard, signal lights, safety devices, adjustable contacts geared to the oscillograph drum, etc., etc., the main electrical circuits will now be described in simplified form, then the results obtained, and finally the computations.

The electrolysis circuit. (Fig. 2). The three "cell-resistances" *Ur*, *Mr*, and *Lr* were adjusted once for all to be equal to the resistance through the electrolytic cell and leads *via* the upper, middle, and lower cathode respectively. Except while the oscillograph shutter was open, contacts were maintained between *Ur* and the "upper rheostat", *Mr* and the "middle rheostat", and *Lr* and the "lower rheostat"; these three rheostats were adjusted until the same current flowed through each of the three "cell resistances", by means of an ammeter, not shewn in the figure, which could be switched into series with each of the three rheostats in turn. This adjustment once made, the electrolysis-current could be varied by means of the "main rheostat", though before each electrolysis the equality of the three currents was checked; the source was a large 110 volt storage battery. When the oscillograph opened its shutter, the relays described below connected the upper cathode, instead of the upper cell-resistance, to the upper rheostat, and the same with the other two, thus sending the current through the cell; and oscillograph element No. 1 recorded the potential-difference between the anode and the middle cathode. When the shutter closed, the former connections were automatically restored.

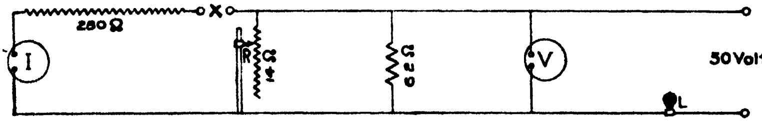


FIG. 3

To avoid induction, carbon lamp rheostats were used throughout, fine adjustment being effected by a slide wire rheostat in series with one of the lamps; the resistance of these lamps had a high temperature coefficient, but as the current flowed through them continuously this did not matter. The "cell resistances" were of manganin, wound non-inductively, and the leads to and from the cell, and from one connection to another, ran side by side in pairs. The ammeter used was a Weston Model 45 (150 divisions full scale) provided with suitable shunts; they were calibrated against a copper coulometer, and also by means of a potentiometer and standard ohm; for each electrolysis-current the appropriate shunt was used, so that the reading on the instrument was never less than 100 divisions of the scale.

The voltage-calibration circuit. (Fig. 3). The 32 c.p. carbon lamp *L* allowed about 0.32 amperes to flow from the 50 volt storage battery; thus with no resistance in the slide-wire rheostat *R* the voltmeter shewed about two volts; this was reduced to the desired value by means of *R* and recorded. When the oscillograph shutter opened, contact was automatically made at X, and a line was photographed whose height corresponded to the recorded voltage, as the resistance of 280 ohms in series with the oscillograph element I prevented any drop in voltage when contact was made at X. When the shutter closed again, the connection at X was automatically broken.

To keep the second element of the oscillograph from drawing a horizontal line while the calibration-voltage line was being photographed, a circuit was arranged which sent sufficient current through that element to throw the light spot off the paper from the moment before the shutter opened until just after it closed again.

The voltmeter was a Weston Model 45 with 500 ohms internal resistance, in a series with which was 4500 ohms; the combination was calibrated by the potentiometer, each division corresponded to 0.0206 volts.

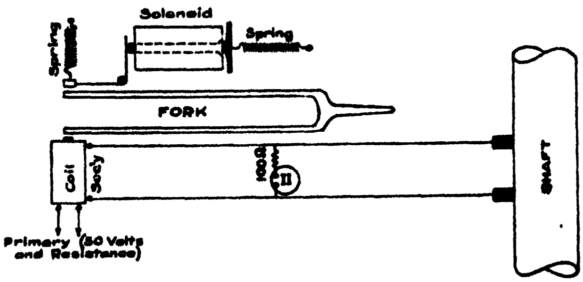


FIG. 4

The oscillograph was the Siemens-Halske two-element instrument used by Redman; a current of 4 milamperes through the element gave a deflection of 45 millimeters on the photographic paper; on most of the oscillograms the deflections ran from 15 to 30 mm.

The tuning-fork circuit. (Fig. 4). A constant current of about one ampere from a storage battery passed through the primary of a small induction coil, the secondary winding of which (7 ohms) was in series with the second element (II) of the oscillograph; the latter was short-circuited for a moment during each revolution of the cathodes, by means of a brass contact attached to the cathode shaft. When the tuning fork was struck (hammer and solenoid) its vibrations induced a sinusoidal current in the secondary of the coil; the resulting wavy line on the photographic paper served to calibrate the time axis, and its interruptions recorded the speed of rotation of the cathodes. To get a nice curve, free from the evanescent distortions which follow the hammer blow, the fork had to be struck about one second before the shutter opened; this was attended to by a contact wheel geared to the oscillograph drum which rotated once for every four revolutions of the drum.

Relay circuits. (Fig. 5). A system of three 20-ohm telegraph relays was used to make the contacts indicated in Fig. 5; the primary of each of them was connected to a dry cell through a resistance so adjusted that the current from the dry cell was insufficient to pull the armature of the relay up to the magnet, but was sufficient to hold it there (against the pull of the relay spring) if a surge of current from some other source had once brought it close; these dry-cell circuits are omitted in the figure.

In the normal state of the relays, with their tongues held away from their magnets by the springs (as in Fig. 5), contact was made in the secondary circuit of Relay II but not in either of the others. When the oscillograph shutter opened, a surge of current from the "opening magnet" of the oscillograph (special connections to which were made for this purpose) excited the magnet of Relay I, which thereupon closed the circuit through the secondary of Relay II to the "electrolysis-magnet"; this circuit remained closed (because of the dry cell on the primary of Relay I) until the "closing-magnet" of the oscillograph was excited and closed the shutter. A surge of current from this "closing-magnet" passed through the primary of Relay III and thus closed the circuit through the secondary of that relay, activated the magnet of Relay II and broke the electrolysis-magnet circuit. To set the relays ready for use again, it is only necessary to break the dry cell circuits for a moment; the tongues are thereupon pulled away from the magnets, and remain away when the dry cell circuits are completed again.

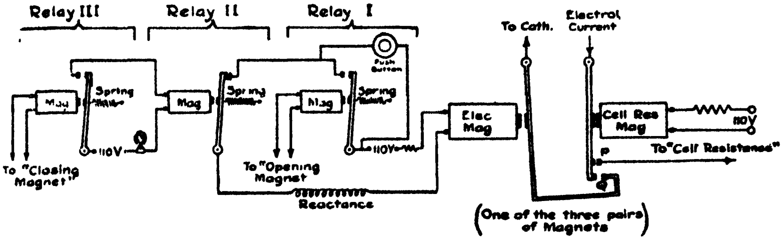


FIG. 5

The "cell-resistance magnet" is supplied with current sufficient to attract its armature and hold it firmly against the contact P; the electrolysis-current then passes via armature and P to the cell-resistance (Fig. 2). When the "electrolysis-magnet" is excited, however, it not only makes the contact at Q, which sends the current through the cathode, but being much stronger than the "cell resistance magnet" it pulls back the armature of the latter and breaks the circuit through P; as, for a moment, the cell-resistance is in parallel with the cell, the contact at P breaks without a spark. There is a "cell-resistance magnet" and an "electrolysis-magnet" for each of the three cathodes; the three electrolysis-magnets are connected in series, and operated from the same relays. In order that the moment at which electrolysis begins might be recorded accurately, a reactance coil was inserted in the circuit leading from the relays to the electrolysis-magnets; this delays the action of these magnets a little, so that the time-voltage curve begins with a short horizontal portion on the zero-voltage line, and rises perpendicularly when the current passes through the cell.

III. MANIPULATIONS TO SECURE A TIME-VOLTAGE CURVE

While the electrolyte was being freed from air, photographic paper was placed on the oscillograph drum, switches were closed to supply current to the oscillograph magnets and motor, fork-hammer, signals, relays, voltage circuit, etc.; the "calibration-voltage" block was put on the mercury switchboard, circuits corrected until the red lights went out, the arc lamp adjusted, voltage set and read, and the switch thrown which permits the oscillograph to open its shutter and record the calibration-voltage line. The oscillograph handles were reset, the current to the calibration-voltage circuit broken, and the zero-voltage line secured.

The electrolyte was then transferred to the cell, the cathode-shaft motor set going, and its speed read on an electric speed-counter and adjusted by means of a rheostat in series with the armature of the motor. The cell thermometer was read, and the temperature of the electrolyte recorded.

The "D. C. electrolysis" block was then put on the mercury switchboard, red lights put out, "relay jack" closed (to complete the dry-cell circuits), and at a signal from the oscillograph the "fork jack" closed, which made it possible for the machine to operate the tuning-fork hammer; immediately after the blow, the "operating jack" was closed, and after waiting a second for the fork to assume steady vibrations, the oscillograph opened its shutter, sent the current through the cell, and photographed the time-voltage curve and the time-calibration curve simultaneously; it then closed its shutter, and the relays stopped the electrolysis.

After two or at most three electrolyses the electrolyte was removed, taking samples for analysis, and the cathodes cleaned. This precaution was necessary because during part of the time of each electrolysis hydrogen was being liberated together with the copper, and the powdery deposit formed under these conditions must obviously affect the thickness of the diffusion film. Under conditions of current, concentration, temperature, and speed of rotation such that comparatively little of this deposit was formed, five time-voltage curves (recorded one under the other on the same photographic paper) which were obtained from five successive electrolyses made without cleaning the cathodes, proved to be almost identical; but under less favorable conditions, there was a distinct difference between the first and the last curve; and in the final determinations, those recorded below, the cathodes were cleaned after every two electrolyses.

Fig. 6 shews one of the time-voltage curves obtained as just described.[1] *AB* is the zero-voltage line, *CD* is the voltage-calibration line, *EF* is the time-voltage curve. Each revolution of the cathodes required 19.5 "waves" of 1/128 second, i.e. the shaft revolved once in 0.152 seconds. The point marked with an arrow, where the curve shews a point of inflexion, was taken to indicate the moment at which the concentration of copper at the cathode reached zero; this is 84.5 "waves", or 0.660 seconds, after the point at which electrolysis began; in Table II this determination would be recorded as $\vartheta = 0.660$.

---

[1] The actual oscillograms were all 21 cm long and 9 cm wide.

IV. LIMITING-CURRENT DETERMINATIONS

When the "limiting-current block" was put on the mercury switchboard, it made contacts to the "push-button" as shewn in Fig. 5; when this button was pressed, it completed the secondary circuit of Relay I and, therefore, sent the electrolysis current through the cell; when the pressure was removed, the current flowed through the cell-resistances again. The block also arranged to have the potential difference between the anode and the middle cathode shewn on the calibration voltmeter.

The current was first adjusted to an amperage somewhat lower than that of the estimated limiting-current, this current was recorded; the button was then pressed, and the potential difference read and recorded. These operations were repeated with successively greater currents, and the observed voltages plotted against the currents; the point at which the curve shewed a sudden increase in steepness gave an approximate value of the limiting-current under the known conditions of concentration, temperature, and rate of rotation of the cathodes. This preliminary determination, however, involved repeated electrolyses, each lasting several seconds, so that the cathodes became covered with a deposit which affected the thickness of the diffusion film; to obtain the definitive value of the limiting-current, therefore, the cathodes were cleaned and a few voltage determinations made with currents closely below and above the provisionally determined value of the limiting current; to cut down the duration of each electrolysis, a lens was held over the voltmeter near the expected reading, and the button was pressed just long enough for the reading to be taken. Thus the final value for the limiting-current was obtained before the cathode surfaces were spoilt; immediately after the last voltage reading a switch was closed which caused the oscillograph to record the speed of rotation of the cathodes, the cell thermometer was read, and a portion of the electrolyte was removed for analysis.

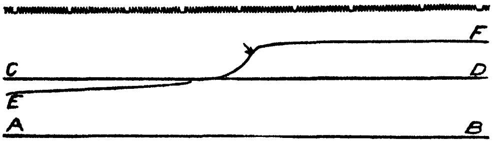


Fig. 6

Results of the Limiting-current Determinations

Fig. 7 shews that, within the limits of experimental error, the limiting current is connected with the concentration of the electrolyte and the rate of rotation of the cathode by the relation

$$(\textit{Lim. current}) \times (\textit{sec. per rev.})^{0.77} = 0.0790 \times (\textit{g. Cu per L.}) \qquad (1)$$

which is the equation to the curve drawn on the figure; the lowest concentration used in these experiments was 0.46 grams of copper per litre and the highest was 4.0 grams.

The form of this relation is that used by Brunner[1], the exponent 0.77 signifies that doubling the peripheral speed of the cathode increases the limiting current to 1.71 times its original value; the theory accounts for this by assuming that the adherent film has been reduced to 1.0/1.71 = 0.59 of its original thickness. Forty unpublished determinations by Redman (18°C, 1.0 to 6.0 g Cu per L) are in good agreement with the exponent 0.55; that is, with Redman's apparatus, doubling the speed of rotation reduced the thickness to two-thirds. The peripherical velocities and the form and dimensions of the cathode in Redman's experiments were almost exactly the same as in mine; but in his, the stationary plates were close to the ends of the rotating electrode, while in my three-cathode cell they were 6.5 cm distant from the middle cathode (for which the limiting currents were obtained).

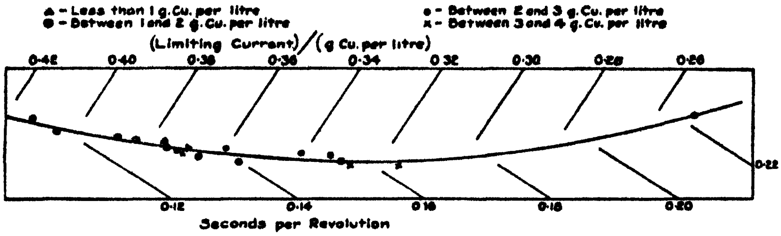


FIG. 7

To test the effect of the position of these stationary plates, two thin circular plates of Redmanol were cut to fit across the cell and perforated in the centres so that they would just slip over the cathodes. These plates were attached by three rods of the same material (at their outer edges, near the anode) to the upper and to the lower stationary plate respectively, so that the central cathode revolved in a cell of its own with stationary plates close to its upper and lower ends. With this arrangement the limiting current was greater (i.e., the film was thinner) than when the plates were at a distance from the central cathode, and the effect of changing the speed of the cathodes was less. The four experiments of Table I fit the equation

$$(\textit{Lim. current}) \times (\textit{sec. per rev.})^{0.41} = 0.206 \times (\textit{g.p.L.}) \qquad (2)$$

TABLE I

1.950 g copper per litre, 18°C.

Sec. per rev.	Limiting current (amp.) obs.	calc. by Eq. (1)	calc. by Eq. (2)
0.172	0.825	0.599	0.823
156	860	643	861
131	911	737	924
117	967	803	968

---

[1] Z. physik. Chem., 47, 56 (1904).

In view of these results, it is obviously illegitimate to assume that there is a diffusion film of uniform thickness over the whole surface of a rotating electrode, unless the latter is kept well away from the stationary ends of the electrolytic cell.

A. COMPUTATIONS OF k AND l FROM THE LIMITING-CURRENTS AND THE TIME-VOLTAGE CURVES.

From the assumptions (*i*) that the diffusion constant k is independent of the concentration of copper in the electrolyte, (*ii*) that the diffusion film is of uniform thickness l cm, (*iii*) that in these strongly acid solutions there is no electrolytic migration of the copper, and (*iv*) that the jump in voltage used to determine the limiting-current occurs when the concentration of copper at the cathode is brought to zero, there follows that the limiting current[1] ($-I'$ amperes), the concentration[2] of copper in the body of the electrolyte (z_0), and the area of the cathode (A sq. cm.), are connected by the equation

$$I' = 96500\, A\, z_0\, k/l = 96500 \times 92.5 \times (g.\ p.\ L) \times k/(31800 \times l) \quad (3)$$

$$\text{whence } k/l = 0.003562 \times I'/(\text{g. p. L.}) \quad (4)$$

Expressing the limiting-current in terms of concentration and speed of rotation (Eq 1) this gives

$$k/l = 0.0002815/(sec.\ per\ rev.)^{0.77} \quad (5)$$

The quantity ϑ (the interval in seconds between the beginning of electrolysis and the first liberation of hydrogen) which is determined experimentally by means of the time-voltage curve as explained above, is related to the electrolysis current ($-I$ amp.) by the equation

$$-96500\, A\, k\, z_0 = I\, l\, (1 - 8/\pi^2\, \Sigma e^{-m^2 a\vartheta}/m^2 \quad [\text{R \& M } 16] \quad (6)$$

where m is written as an abbreviation for $2n+1$, a for $\pi^2 k/4l^2$ and Σ for $\sum\limits_{n=1}^{\propto}$ ·

The two equations (4) and (6) thus furnish two independent relations between k, l, I', and ϑ, so that from a time-voltage curve and the value of I' for the same experimental conditions (which may be found from Eq. 1), both k and l may be computed. If the electrolysis-current be twice the limiting-current, or greater, k can be computed from the time-voltage curve alone, for in that case Eq. (6) may be replaced by

$$I'/I = 0.71835\sqrt{a\vartheta} \quad [\text{R \& M } 22a^3] \quad (7)$$

$$\text{whence } k = 1.616 \times 10^{-5}\, I^2\vartheta/(g.\ p.\ L.)^2 \quad (8)$$

But if the electrolysis-current be less than twice the limiting-current, Eq. (6) becomes

---

[1] The convention adopted in the "mathematical theory" and followed here, is that a current is reckoned positive if it *increases* the concentration-at-the-electrode of the substance whose diffusion-constant is represented by k. At the cathode in solutions of copper sulphate, the current *decreases* the concentration of copper; the "limiting-current" as defined above thus corresponds to $-I'$ of the equations, and the electrolysis current to $-I$.

[2] The number of equivalents of copper in one cubic centimetre of the solution taken for electrolysis is represented by z_0; the number of grams of copper in a litre of the same solution by ($g.\ p.\ L$); thus $(g.\ p.\ L) = 31800\, z_0$.

[3] Since, when $z = 0$, $(z\text{-}z_0)/Cl = I'/I$; see R. & M., Eq. 24.

$$I'/I = 1 - 8e^{-a\vartheta}/\pi^2 e^{-a\vartheta} \quad [\mathrm{R\ \&\ M\ 17}] \tag{9}$$

and both time-voltage curve and limiting-current determination are needed.

The actual computations are most conveniently carried out by means of a table giving *log* (I'/z_0) for different rates of revolution of the cathode, and a second table giving *log at* for different values of log I'/I.

VI. RESULTS OF THE COMPUTATIONS

1. When the electrolysis-current is twice the limiting-current or greater, the theory predicts that the time needed to bring the concentration of copper at the electrode to zero will be independent of the rate of rotation of the cathode. This follows at once from equation (7) by substituting for I' its value from equation (4) and for a its value, $\pi^2 k/4l^2$; the expression for ϑ so obtained, viz $\vartheta = factor \times (g.\ p.\ L.)^2 \times k/I^2$, does not contain l and is therefore independent of the rate of rotation of the electrode (see Eq. 5).

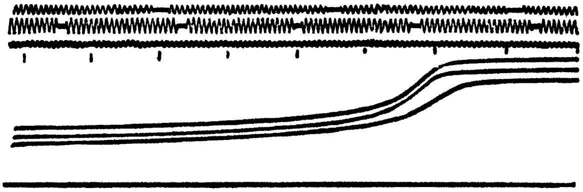


FIG. 8

Figure 8 gives the time-voltage curves for three electrolyses carried out one immediately after the other, with the same electrolyte ($g.\ p.\ L. = 1.910$) and the same current ($-I = 1.180$); the cathode speeds were 0.280, 0.184, and 0.110 seconds per revolution respectively[1]. From these data, the values of I'/I, viz 0.341, 0.471, and 0.700, were computed. The values of ϑ read from the oscillogram are 0.644, 0.648 and 0.700 seconds respectively—the first two equal, within the limits of error of the experiments, and the third greater, as predicted.

2. Table II gives the experimental data for 42 time-voltage curves, and the value of k computed from each; the determinations are arranged in order of increasing I'/I in the table, and the values of k are plotted against copper-concentration in Fig. 9. In neither case is there positive evidence of a trend in the values of k, although the graph hints at a decrease with increasing concentrations; all the determinations lie around $k = 4.0 \times 10^{-6}$. Rejecting the three extreme values (one below and two above the mean), the remaining thirty-nine give $k = (4.00 \pm 0.07) \times 10^{-6}$; thus the dispersion, or "probable error" is one and three-quarters percent of the mean value, 19 of the determinations shew less.

An error of one percent in the copper-determination or in the electrolysis-current would introduce an error of two percent in k; an error of one percent

---

[1] The interruptions on the third tuning fork curve, which are quite distinct on the original oscillogram, have their positions indicated by pen marks in this reproduction.

TABLE II

Film No.	*(g. p. l.)*	*Sec. p. r.*	$-I$	I'/I	$a\vartheta$	ϑ	10^6k
293	2.556	0.146	2.667	0.334	0.216	0.227	3.98
302 (a)	1.910	0.280	1.180	0.341	0.225	0.644	3.98
183	1.600	0.138	1.583	0.367	0.261	0.261	4.13
487	0.460	0.141	0.416	0.395	0.302	0.316	4.18
128	3.795	0.150	3.077	0.420	0.342	0.383	4.07
175	1.200	0.139	1.032	0.420	0.342	0.323	3.68
182	1.600	0.133	1.410	0.424	0.349	0.316	3.97
130	3.875	0.144	3.185	0.428	0.355	0.348	3.80
424	3.440	0.133	2.968	0.433	0.363	0.336	4.04
129	3.875	0.144	3.137	0.433	0.363	0.356	3.79
132	3.875	0.141	3.198	0.433	0.363	0.348	8.83
126	3.795	0.149	2.983	0.436	0.368	0.398	3.97
127	3.795	0.141	2.983	0.455	0.401	0.391	3.90
301(b)	2.244	0.223	0.204	0.468	0.424	0.844	3.92
302(b)	1.910	0.184	1.180	0.471	0.430	0.648	4.00
173	1.200	0.121	1.020	0.472	0.432	0.350	4.10
291	2.556	0.142	1.930	0.472	0.432	0.445	4.07
486	0.460	0.139	0.356	0.501	0.486	0.481	4.04
440	3.924	0 131	2.900	0.512	0.507	0.453	4.00
422	3.440	0.131	2.488	0.523	0.530	0 480	4.05
98	1.566	0.141	1.061	0.528	0.541	0.571	4.22
100	1.578	0.139	1.061	0.536	0.558	0.547	4.00
439	3.924	0.133	2.730	0.537	0.560	0.523	4.08
99	1.572	0.138	1.061	0.538	0.562	0.555	4.08
289	1.460	0.140	0.975	0.538	0.562	0.578	4.15
181	1.600	0.133	1.085	0.551	0.591	0.522	3.86
96	1.550	0.134	1.012	0.569	0.632	0.584	4.00
421	3.440	0.133	2.185	0.589	0.681	0.630	4.04
176	1.200	0.121	0.804	0.599	0.704	0.562	4.04
655	2.400	0.151	1.462	0.599	0.704	0.789	3.99
664	2.802	0.147	1.592	0.610	0.732	0.773	3.96
296	3.332	0.143	1.925	0.612	0.737	0.750	3.98
670	2.753	0.139	1.543	0.645	0.826	0.851	4.21
285	1.460	0.143	0.796	0.649	0.837	0.848	3.96
423	3.440	0.131	1.990	0.654	0.851	0.725	3.81

TABLE II (continued)

Film No.	*(g. p. l.)*	*Sec. p. r.*	$-I$	I'/I	$a\vartheta$	ϑ	10^6k
650	2.050	0.134	1.136	0.671	0.901	0.852	4.07
680	1.708	0.127	0.952	0.695	0.977	0.832	4.00
663	2.802	0.137	1.465	0.699	0.991	0.990	3.80
302 (c)	1.910	0.110	1.180	0.700	0.994	0.700	4.13
694	1.378	0.133	0.726	0.710	1.028	0.963	4.10
679	1.708	0.125	0.921	0.727	1.088	0.922	4.08
301 (a)	2.244	0.111	1.204	0.801	1.405	0.977	4.01

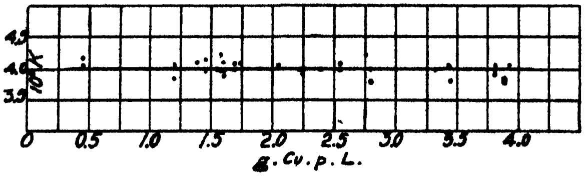


FIG. 9

in reading ϑ would cause an error of one percent in k; an error of one percent in the rate of rotation of the cathode might cause an error of 1.2 percent in k. A few determinations made at varying temperatures shew that an error of 0.1°C in the temperature of the electrolyte (which affects l as well as k) would cause an error of 0.6% in k. Thus it seems justified to adopt the value $k = 4.0 \times 10^{-6}$ as the diffusion constant of copper in 7.6 normal sulphuric acid at 18°C, for concentrations from 0.5 to 4.0 grams per litre; and to conclude that the predictions of the mathematical theory for electrolysis with constant currents are borne out by the experiments within the limits of experimental error.

3. To test the theory under unfavorable experimental conditions, two electrolyses were carried out with very slow rotation of the cathode, five with the cathode stationary, and four in a rectangular glass cell with flat copper electrodes 6.5 cm × 7.5 cm, which fitted closely to the sides of the cell and were 2.0 cm apart; Eq. (8) was used to calculate k. The results are given in Table III; they agree with the others as well as could be expected, when the probability of accidental motion of the liquid is taken into consideration.

VII. EFFECT OF VARIATION OF l ALONG THE CATHODE

The very noticeable increase of the limiting-current brought about by placing stationary plates close to the two ends of the middle cathode (pg.404), must be due to their action in retarding the circular motion of the electrolyte, which would increase the friction at the surface of the revolving cathode, and, therefore, decrease the thickness of the adherent liquid film; it follows that when the plates are close to the ends of the cathode, the film must be thinner at its ends than at its middle.

TABLE III

No.	*g. p. l.*	*Sec. per rev.*	$-I$	ϑ	10^6k
371	1.938	0.582	1.379	0.516	4.22
372	1.938	0.781	1.408	0.488	4.17
382	1.868	stationary	1.073	0.688	3.67
354	1.868	"	1.110	0.656	3.75
363	1.868	"	1.197	0.590	3.92
360	1.868	"	1.404	0.477	4.36
361	1.868	"	1.486	0.406	4.15
366	1.838	flat cell	1.023	0.219	3.92
365	1.838	"	1.038	0.219	4.04
364	1.838	"	1.195	0.149	3.64
363	1.838	"	1.337	0.125	3.83

The theory of electrolysis when the thickness of the film is different at different points of the electrode was not dealt with in the paper on "mathematical theory", and it cannot be treated quantitatively unless the distribution of the different thicknesses along the electrode is known. It would seem that some theory of this distribution should be found in treatises on hydrodynamics, but I have not been able to find one; and in what follows have restricted myself to a rough qualitative treatment of the problem.

Consider the surface of the vertical cathode to be divided into a number of infinitesimal horizontal strips, each passing completely around the cathode, and each of the area A_1; since the strips are parallel to the plates, the film will have the same thickness opposite every part of the same strip, its thickness will be least for the end strips, will increase towards the middle, and will be the same for pairs of strips situated symmetrically with respect to the middle of the cathode. The suffix $_1$ is used to indicate the middle strip, and $_2$ one of the end strips; thus, $l_1 > l_2$.

At any moment during electrolysis the whole surface of the cathode mus be at the same electrical potential; the *i.r* drop from anode to cathode is the same for each strip; and if it be assumed that the rest of the potential difference (viz: concentration-voltage and overvoltage) depends merely on the concentration of copper in the electrolyte at the surface of the cathode, it follows that at any moment during electrolysis the concentration must be the same opposite every strip. This hypothesis is in accordance with experimental results obtained by Mr. A. R. Gordon, a preliminary account of which has already been published[1].

From the beginning of the electrolysis until $a_2.t = 0.5$ (at which moment at for every other strip[2] will be less than 0.5), the rate of fall of concentration at the cathode is independent of l and is proportional to the current density (R & M 22); hence in order to maintain the same concentration opposite every strip, the current density must have the value $-I/A$ at every point on the cathode until $a_2.t = 0.5$; and if the concentration of copper falls to zero before that moment, it is obvious that the variation in l along the cathode can have no effect on the value of ϑ. From then on, however, the current-density at the end strips must be appreciably greater than that at any other strip (including the middle strip) where the film is thicker than at the end strip; but as the electrolysis-current is maintained at constant intensity, this means that from $a_2.t = 0.5$ on, the current-density at the middle strip must fall, and that at the end strips increase. Equations have been developed for following the concentration changes at the cathode when the current-density changes with the time according to any given law, but as the distribution of l is not known, they cannot be made use of.

---

[1] W. Lash Miller: Franklin Institute, Centenary Publications, September, (1924).

[2] $at = \pi^2kt/4l^2$

Two propositions, however, can be established:

(*i*) There must be some constant current-density, $-B_1/A_1$ amperes per cm.², less than $-I/A$ (the actual current density at the middle strip when $t = 0$) but greater than the actual current density at the middle strip when $t = \vartheta$, which, if maintained at the middle strip from $t = 0$ to $t = \vartheta$, would just bring the concentration at the strip to zero at the moment $t = \vartheta$. Thus

$$B_1\,A/IA_1 < 1.0 \tag{10}$$

(*ii*) The limiting-currents for each strip, viz: $-I_1$, $-I_2$, etc., are related to $-I'$, the limiting-current for the cathode as a whole, by the equations:

$$I'_1\,.\,l_1/A_1 = I'_2\,.\,l_2/A_1 = \ldots = I'\,.\,L/A;\ \text{whence}\ I'/I'_1 = l_1A/L\,.\,A_1 \tag{11}$$

This follows from Eq. (6), since by definition the limiting currents make $z = 0$ at the electrode, when $t = \propto$. In this equation, L is the fictitious film thickness introduced by making the false assumption that the film is of uniform thickness throughout.

By means of equations (10) and (11), a lower limit to the value of l_1/L may be obtained from the data of Table IV, as follows:—Each value of k given in this Table was computed by looking up the value of at that corresponds to the fraction I'/I and multiplying it by $4L^2/\pi^2\vartheta$; the true value of k would be found by looking up the value of at that corresponds to the fraction I'_1/B_1 and multiplying it by $4l^2_1/\pi^2\vartheta$. Near $at = 0.8$ (an average value for Table IV) the ratio of these two values of at is close to the 2.2 power of the ratio of the two fractions; hence

$$\frac{k\ (table)}{k\ \ (true)} = \left(\frac{I'\cdot B_1}{I\cdot I_1'}\right)^{2.2}\cdot\left(\frac{L}{l_1}\right)^2 = \left(\frac{B_1\cdot A\cdot l_1}{I\cdot A_1\cdot L}\right)^{2.2}\cdot\left(\frac{L}{l_1}\right)^2 = \left(\frac{B_1\cdot A}{I\cdot A_1}\right)^{2.2}\cdot\left(\frac{l_1}{L}\right)^{0.2} \tag{12}$$

so that, by Eq. (10), $(l_1/L)^{0.2}$ must be at least equal to the ratio of the values of k.

While the results of Table IV differ rather widely, due to the difficulty of fitting the plates in exactly the same positions after each electrolysis, yet every experiment with rotating cathode gives a higher value of k than the three with cathode stationary; the average with rotating cathode is 4.14×10^{-6}, with stationary[1] cathode 3.83×10^{-6}, and the quotient 1.08. Using this quotient for want of a better, (and remembering that B_1A/IA_1 is less than unity) Eq. (12) gives 1.47 as the minimum value of l_1/L; as L (calculated by Eqs. 2 and 4) runs from 2.3×10^{-3} to 2.7×10^{-3}, this would make the film at the middle of the cathode a little thicker than in the experiments of Table II; and as it seems unlikely that the friction of the plates could actually *increase* l at any point of the rotating electrode, it may be concluded that the thickness of the film at the centre of the cathode is the same whether the plates are close to its ends, or are separated by the lengths of the upper and lower electrodes.

TABLE IV

No.	*g. p. l.*	*Sec. per rev.*	$-I$	I'/I	$a\vartheta$	ϑ	10^6k
88	1.950	0.126	1.508	0.623	0.766	0.414	3.92
89	”	0.121	1.522	0.627	0.776	0.445	4.30
87	”	0.129	1.393	0.666	0.887	0.516	4.13
90	”	0.121	1.379	0.692	0.967	0.547	4.24
81	”	0.172	1.173	0.703	1.004	0.724	4.04
79	”	0.148	1.173	0.749	1.172	0.801	4.35
86	”	0.131	1.223	0.756	1.201	0.711	4.16
92	”	0.124	1.237	0.764	1.234	0.648	3.86
80	”	0.164	1.095	0.769	1.256	0.989	4.18
91	”	0.123	1.166	0.813	1.464	0.844	4.26
85	”	0.126	1.137	0.826	1.538	0.883	4.17
82	”	stationary	0.981	.....	.....	0.922	3.78
83	”	”	1.138	.....	.....	0.703	3.88
84	”	”	1.202	.....	.....	0.625	3.84

Thus, although the experiments of Table IV are obviously not accurate enough for individual computation, they serve to shew that the disturbing influence of the stationary plates does not extend far along the cathode, and that when the plates are removed to the ends of the cell, as in the experiments of Table II, the film may be regarded as of uniform thickness throughout.

VIII. EFFECT OF AN UNSYMMETRICAL ELECTROLYTIC FIELD

The first and second experiments of Table V were made exactly as those of Table II; in the third and fourth no current was sent through the upper and lower electrodes. Owing to the low *i.r* drop through the electrolyte, and to the high polarization from the very first moment of electrolysis, one would expect the current to distribute itself fairly uniformly over the cathode, in spite of the fact that the anode was three times as high. The results bear out this conclusion, and shew that the provision of additional cathodes is not so important as it is to keep the working cathode away from the ends of the cell. A further experiment, in which current was sent through all three cathodes, but the upper cathode (instead of the middle cathode) was connected to the oscillograph, gave $k = 4.38 \times 10^{-6}$; while a duplicate in which the middle cathode was connected gave 4.18×10^{-6}, shewing again that it is more necessary to keep the hydrostatic field uniform than the electric.

---

[1] This value is lower than the average of the more reliable determinations of Table II; but it seems better to compare values which were obtained during the same series of determinations and which, therefore, may be assumed to be affected with the same constant experimental errors. Substitution of the value $k = 4.0 \times 10^{-6}$ does not alter the final conclusion.

TABLE V

No.	*g. p. l.*	*Sec. per rev.*	$-I$	I'/I	$a\vartheta$	ϑ	10^6k
71	2.552	0.133	1.236	0.772	1.269	1.172	4.04
72	"	"	"	"	"	1.164	4.01
73	"	"	"	"	"	1.195	4.12
74	"	"	"	"	"	1.191	4.10

Summary

The paper describes apparatus and circuits for recording the potential difference over an electrolytic cell during the first second or so of an electrolysis, and for calibrating the oscillographic record with respect to the time and to voltage. The electrolyses described were carried out at 18.0°C. with solutions of copper sulphate in maximum-conducting sulphuric acid.

To secure uniform fluid friction over the whole surface of the revolving cathode, the latter was mounted on a vertical shaft between two auxiliary electrodes of the same dimensions; to secure a uniform electrolytic field, the three electrodes were supplied with currents of the same intensity; only the central cathode was connected to the oscillograph.

The rate of revolution of the cathode-shaft was recorded on the oscillogram, and an empirical relation was established between the limiting-current, the rate of revolution, and the concentration of the electrolyte.

From this relation, if the diffusion-constant of the copper be known, the equations of "The mathematical theory of the changes of concentration at the electrode" can predict the time that must elapse before hydrogen will be liberated by a known current passing through a solution of known concentration into a cathode revolving at a known rate. Assuming $k = 4.0 \times 10^{-6}$, these predictions agree with the time intervals recorded by the oscillograph within the limits of experimental error. Results of electrolyses between flat copper electrodes were also in accordance with the predictions.

The effect of unequal friction between the electrolyte and different parts of the same cathode surface is discussed, and evidence adduced that errors from this source have been avoided in the apparatus employed.

The apparatus described has grown out of that employed by Mr. L. V Redman in this laboratory in 1907-10; it has been rebuilt, tested, and re modelled many times since then. I wish to express my obligations to Professor W. Lash Miller under whose direction this series of investigations has been carried out, to Mr. L. V. Redman from whom I received my first instruction in the technique of these measurements, to Mr. H. A. G. Willoughby, Mr. A. D. Hone and Mr. H. R. Brant, who worked with me in constructing and improving the complicated apparatus, to Dr. S. Dushman for assistance in the earlier measurements and to Mr. A. R. Gordon for cooperation in the final determinations.

The University of Toronto,
Electrochemical Laboratory,
December, 1925.

THE EFFECT OF ULTRA-VIOLET LIGHT ON THE OXIDATION OF SODIUM SULFITE BY ATMOSPHERIC OXYGEN*

BY RALPH B. MASON AND J. H. MATHEWS

Dilute solutions of sodium sulfite are readily oxidized by atmospheric oxygen. The rate of this reaction is quite dependent on the presence of minute traces of foreign substances, which may either retard[1] or speed up the reaction[2].

Under the influence of violet light sulfurous acid[3] is changed to sulfuric acid. Loew[4] exposed sealed tubes containing dilute solutions of sulfates, sulfites, sulfurous acid and sulfuric acid to the bright summer sun for three months. The sulfurous acid remained clear for two months, but after that sulfur was deposited and sulfuric acid formed. The other solutions remained unchanged. Sodium sulfite solutions are oxidized more rapidly in ultra violet than in ordinary light. Mathews and Weeks[5] have investigated the effect of certain negative catalysts upon the rate of this photochemical reaction.

Several theories have been advanced as to why certain oxidations proceed more rapidly in ultra-violet light than in ordinary light. Some contend that ozone or hydrogen peroxide is formed from the oxygen and this in turn oxidizes the substance. Chlopin's[6] experiments show that the ordinary moist air of a room, after subjection for a few minutes to the action of ultra-violet light, contains traces of ozone, hydrogen peroxide, and nitrogen trioxide. Others think that the oxygen is ionized by the action of light and that this ionized oxygen is more active than ordinary oxygen. In their work on activated air, Bredig and Pemsel[7] exposed oxygen to ultra-violet light, X-rays, uranium rays, and phosphorus one-fourth second before it was passed into a solution of sodium sulfite and found no increase in the rate of the reaction.

The purpose of the work to be described was to determine, if possible, the effect of the ultra-violet light alone on the oxidation of sodium sulfite solutions when certain catalysts were present. Early experiments indicated clearly that the reaction was mainly a "dark reaction". The term "dark reaction" is used here and elsewhere to indicate the reaction that takes place in the diffused light of the laboratory. The rate of the reaction is no slower in absolute darkness. The difference between the rate of the total reaction and the rate of the reaction in the dark was taken as the rate of the light reaction. Absorption spectrograms were made for all reacting substances, products and catalysts.

---

*Contribution from the laboratory of physical chemistry, of the University of Wisconsin.

[1] Bigelow: Z. physik. Chem., **26**, 493 (1898).

[2] Titoff: Z. physik. Chem., **45**, 641 (1903).

[3] Eder: "Photographie bei künstlichem Licht," 332.

[4] Am. J. Sci., (2) **49**, 368 (1870).

[5] J. Am. Chem. Soc., **39**, 635 (1917).

[6] J. Russ. Phys. Chem. Soc., **43**, 554-561 (1911).

[7] Eder's Jahrbuch Phot., **1900**, 541.

Preparation of Materials

Sodium Sulfite. Sodium sulfite was prepared by three different methods, Since there was no difference in behavior between these samples, and Merck's blue label sulfite, the latter was used in the final experiments.

Water. The water used was distilled from an alkaline permanganate solution then from barium hydroxide in an all-metal still, provided with a trap and a block tin condenser. It had a conductivity of 2 to 2.4×10^{-6} mhos at 25°C.

Catalysts. The phenol was purified by recrystallizing three times. The copper sulfate, hydroquinone and sugar were recrystallized from conductivity water. No attempt was made to purify the quinine sulfate.

Source of Ultra-violet Light. A quartz mercury vapor lamp was used in the preliminary experiments as a source of ultra-violet light but was later replaced by the cadmium spark which could be brought closer to the reaction flasks, thus giving a greater intensity of ultra-violet and one much easier to control. The alternating current of the laboratory was stepped up through a one K.W. transformer and passed between two cadmium electrodes 5 mm. in diameter and 4 mm. apart. A variable resistance, inserted in the primary circuit, was used to keep the current constant at 3.5 amperes. In parallel with the secondary circuit were four large glass plate condensers in series. This equipment gave an intense, fat spark and the reaction was more rapid than with the mercury vapor lamp.

Reaction Flasks. The spherical transparent quartz reaction flasks were placed equidistant from the source of ultra-violet light, the distance from the light to each flask being equal to the focal length of the flask when filled with water.

Temperature Control. Since the oxidation of sodium sulfite is not a pure photochemical reaction but one which also takes place in the dark, it was necessary to keep the temperature more constant than for a pure photochemical reaction. By means of a small gear pump the water from the thermostat (kept at 25°) was forced into a reservoir above the reaction flasks and was then distributed in a thin film over the outer surface of the flasks from hollow, perforated block tin collars. The variations of temperature in the reaction flasks were less than .1°C from 25°C.

Air. The air from the pressure line in the laboratory was purified by passing through soda lime, sulfuric acid, sodium hydroxide and conductivity water. It was then passed into a five gallon bottle which acted as a buffer to small fluctuations in pressure. The flow of air through the reaction flasks was controlled by two very fine needle valves and the rate of flow measured by flow meters[1]. The rate of flow was 60 liters per hour, except as otherwise stated. The air was forced through small glass tubes and bubbled up through the solutions in the quartz reaction flasks. These tubes were made by cutting a long tube in the middle and grinding the ends. With tubes so prepared the rates of the reactions in the two flasks were equal for a given volume of air per minute. Experiment showed that the shape and size of the bubble influenced the rate of the reaction, hence the necessity of delivering the air in exactly the same manner to both flasks.

---

[1] Benton: J. Ind. Eng. Chem., **11**, 623 (1919).

In order to keep the solutions well mixed, mechanical stirrers were first used but it was found later that the bubbling of the air through the solutions caused sufficient mixing.

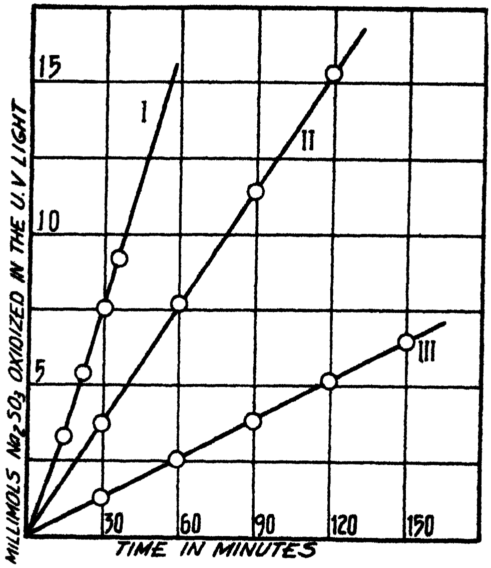


Fig. 1

I. 30 Liters pure O_2 per hour
II. 60 Liters air per hour
III. 30 Liters air per hour
Temperature 30°C

A large size Krüss spectrograph containing quartz lenses and prism was used for making the absorption spectrograms. The ends of the absorption cell were transparent plates (optical flats) of quartz. Each solution used was placed in the absorption cell and exposed for fifteen seconds and a graph was made from the spectrograms for the absorption of the solution for varying lengths of the cell (10, 30, 60, and 100 mm.).

Procedure. For each determination an approximately .1 molar solution of the purified sodium sulfite was prepared. 150 cc of this solution were introduced into each of the quartz flasks. The flasks were placed equidistant from the cadmium spark and the time of starting the spark noted. At intervals of 20 to 30 min. 5 cc portions were withdrawn from the flasks by means of a pipette and run into an excess of a .03 N solution of sodium thiosulfate. The two flasks were first standardized against each other in the laboratory light.

The flow of air was varied very slightly until the rate of reaction in the two flasks was the same. It was possible to duplicate these runs, that is, keep the rate of reaction in the two flasks equal but it was impossible to duplicate from day to day the total time required for a run. This would vary from four to five minutes in a three hour run, so flask No. 1 was used as a control. Spectrograms showed that a thick glass plate cut out all the ultra-violet light. The rate of reaction behind a thick glass plate was no faster than in total darkness, hence the difference in the rate of reaction in the flask in ultra-violet light and the rate of reaction in the flask shielded from the ultra-violet light was considered to be due to the ultra-violet light alone.

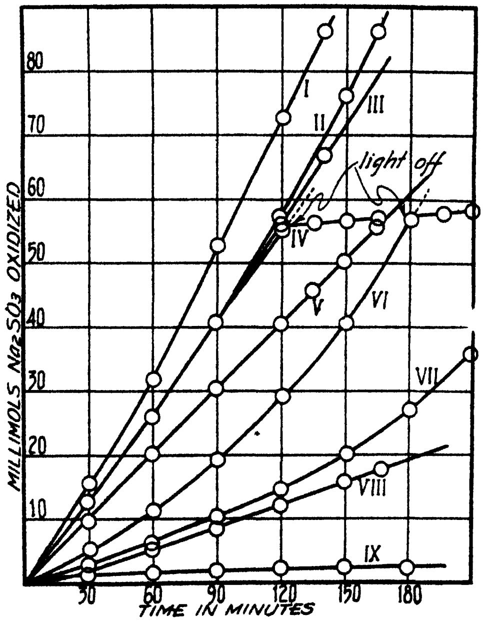


FIG 2

I. Control
II. $CuSO_4$ in Light and Dark
III. Control in dark
IV. Rubber in light
V. Rubber in dark
VI. .001 Hydroquinone in light
VII. .002N Hydroquinone in light
VIII. Rubber catalyst made in U. V. light and used in the dark
IX. .001N and .002N Hydroquinone in dark

The rate of oxidation in the dark at 0°C is not much slower than the rate of oxidation at 30°C (1:1.32). This is due no doubt to the fact that oxygen is more soluble at 0° than at 30°.

Pure CO_2 bubbled through the solution stopped both the dark and light reactions. Increasing the rate of flow of air through the solution increased the rate of oxidation. The rate of oxidation in the light was more than doubled when the rate of flow was sixty liters per hour instead of thirty liters (See Fig. 1). Pure oxygen speeded up the rate of reaction.

In the preliminary experiments it was observed, after a run was nearly completed and the ultra-violet light turned off, that the rate of oxidation in the flask previously exposed to the ultra-violet light was many times slower than the rate of oxidation in the other flask. This phenomenon indicated the building up of a strong negative catalyst by the light, which had little influence on the light reaction but a powerful influence on the dark reaction. After a long search, the rubber stoppers in the trap of the condenser were found to be the cause of this peculiar behavior. Water prepared in a still having no rubber stoppers did not show this phenonemon. A well-washed rubber stopper placed in conductivity water and boiled for a few minutes would dissolve enough to act as a catalyst. The break in the curve (Fig. 2) indicates the point where the light was turned off. If there was no rubber constituent in the solution the rate would have been the same as in the flask not exposed to the light. Pure gum rubber acted in the same manner as the rubber stopper, indicating that it was the rubber and not the substances used to vulcanize the rubber which caused this behavior. Water containing traces of rubber showed a banded absorption in the ultra-violet region, with a slight transmission around 2300 Å (Fig. 4).

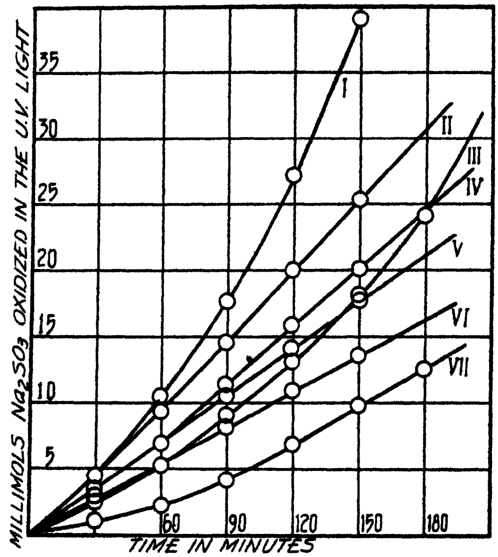


FIG. 3

I. .001N Hydroquinone
II. .001N Phenol
III. .002N Hydroquinone
IV. Control
V. Rubber and pure gum
VI. Sugar
VII. .001N Quinine Sulphate

The effects of different catalysts on the light reactions are shown graphically in Fig. 3. The number of millimols of sodium sulfite oxidized in the light alone are plotted against time in minutes. It will be noticed that .001 N hydroquinone and .001 N phenol acted as positive catalysts to the light reaction. The .002 N hydroquinone did not act as a positive catalyst until the reaction was nearly one-third over. All the other substances tried acted as negative catalysts; copper sulfate stopped the light reaction entirely. Hydroquinone in either .001 N or .002 N solution almost entirely stopped the dark reaction, (See Fig. 2) while quinine sulfate and phenol were somewhat less effective. $CuSO_4$ had practically no effect on the dark reaction.

Titoff[1] found copper sulfate to be a powerful positive catalyst, but his solutions were very dilute as compared with the .1 M sulfite solution used here. Milbauer and Pazourek[2] found that copper salts had little or no effect upon catalysts when the solutions were very pure and dilute.

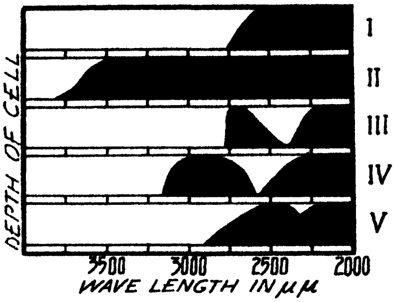


Fig. 4

I. Sodium sulfite
II. Quinine sulfate
III. Phenol
IV. Hydroquinone
V. Rubber

In Fig. 4 are shown the graphs made from the spectrograms. A thick glass plate cut out all the ultra-violet while the sodium sulfate, sugar and copper sulfate solutions showed only slight absorption in the extreme ultra-violet. Quinine sulfate absorbed some of the blue in the visible end of the spectrum as well as all the ultra-violet. Sodium sulfite solution and rubber showed strong absorption in the ultra-violet while phenol and hydroquinone showed a banded absorption with transmission at 2500 and 2600 Å respectively. The solutions containing hydroquinone and quinine sulfate were opalescent in the ultra-violet light and the one containing hydroquinone turned a permanent orange color before the reaction was over.

Discussion

There does not appear to be any simple relation between the absorption of light by the catalyst and its effect upon the rate of the reaction. Copper sulfate absorbed only the extreme ultra-violet and acted as a negative catalyst to the light reaction and did not appreciably affect the rate of the dark reaction. Quinine sulfate absorbed all the ultra-violet light and acted as a negative catalyst both to the light and dark reactions.

---

[1] Z. physik. Chem., **45**, 641 (1903).

[2] Bull., **31**, 676-8 (1922).

The fact that the light reaction increased with the rate of flow of air seems to indicate that the oxygen of the air was made much more active by the ultra-violet light and this active oxygen in the form of peroxide or ozone in turn oxidized the sulfite.

Hydroquinone acted as a powerful negative catalyst to the dark reaction. On the other hand, the rate of oxidation of the sulfite in the ultra-violet light was increased and the reaction was practically all photochemical.

Rubber acted as a weak negative catalyst to the light and dark reactions but became a strong negative catalyst to the dark reaction after exposure to ultra-violet light. The behavior of the hydroquinone may be explained by the formation of an intermediate complex with the sulfite, this intermediate compound being oxidized by ordinary oxygen. Under the influence of the ultra-violet light either the complex compound was broken down into the original constituents or the active oxygen produced by the light was active enough to oxidize the complex compound and change the sulfite to sulfate.

Summary

1. The rate of oxidation of an aqueous sodium sulfite solution is highly dependent on the rate at which oxygen is bubbled through the solution. The shape and size of the bubble greatly influence the rate of oxidation.

2. Pure oxygen and ozone greatly increase the rate of reaction both in the dark and in the light. The rate of the light reaction is more than doubled when the flow of air is increased from 30 to 60 liters per hour.

3. Hydroquinone and phenol in .001 N solutions act as positive catalysts to the light reaction while sugar, quinine sulfate, rubber, and copper sulfate, act as negative catalysts to the light reaction.

4. Our experience with contamination due to some constituent of rubber re-emphasizes the necessity for the exercise of the utmost care in the exclusion of all possible contaminations in the study of photochemical effects.

5. There is no apparent relationship between the light absorption of the catalysts and their action upon the photochemical oxidation of sodium sulfite.

Madison, Wis.
December, 1925.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *Vol. VI. By J. W. Mellor. 25 × 16 cm; pp. x+1024. London and New York: Longmans, Green and Co., 1925. Price: 63 shillings; $20.00.* We welcome the sixth of these remarkable volumes. This volume finishes the discussion of carbon, taking up the carbonates and carbon bisulphide. Well over eighty-five percent of the book is devoted to silicon. As was the case with the other volumes, this one is a treasure-house of interesting facts.

"Chamberlin estimated that 1,620,000,000 tons of carbon dioxide are withdrawn annually from the atmosphere in the formation of sedimentary rocks, p. 4. "It will be noticed that all animal and vegetable life is dependent upon the carbon dioxide$\longrightarrow$carbon reaction, which in turn is dependent upon the sun's energy. There is a kind of closed cycle, an alternation of oxidations and deoxidations:

Sun's energy stored——plants feed

$$\xrightarrow{\text{deoxidation}} \text{C}$$

$$\text{CO}_2 \xleftarrow[\text{oxidation}]{}$$

Energy dissipated——animals and plants breathe etc.,

maintained by a continuous supply of energy from the sun. If the supply should cease' the deoxidation of carbon dioxide would stop and the present conditions of life on the earth would come to an end because the available carbon would be transformed into unavailable carbon dioxide," p. 13.

The Poison Valley or the Valley of Death in Java is an old volcanic crater with fissures from which are evolved large quantities of carbon dioxide which fill the valley as water fills a lake. The flow is apparently intermittent because sometimes scarcely a trace of gas can be found, while at other times it fills the valley. The valley is about half a mile in circumference and is oval. The depth is from thirty to thirty-five feet. The bottom is quite flat, with no vegetation, and is covered with the skeletons of human beings, tigers, pigs, deer, peacocks, and all sorts of birds. "The Death Gulch of the Yellowstone Park is another such valley, where it is said that grizzly bears are sometimes found suffocated to death by the carbon dioxide which issues from the ground. The Laacher Sea is the water-filled crater of a prehistoric volcano, and near by is a depression filled with carbon dioxide. Birds and insects flying in this region are suffocated", p. 7.

"According to R. Brimmeyr, when carbon dioxide is separated from hydrogen by a moist bladder, more carbon dioxide diffuses to the specifically lighter gas then conversely; and with a dry porous partition, less carbon dioxide diffuses to the specifically lighter gas than conversely. Wiesner and Molisch also found that carbon dioxide diffuses through vegetable membranes more rapidly than hydrogen, oxygen, or nitrogen," p. 24. Carbon dioxide should diffuse more slowly through pores than hydrogen. When water is present and the diffusion is chiefly, or perhaps entirely, through the water, the solubility relations are the decisive ones.

The presence of air interferes with the liquefaction of carbon dioxide much more than can be accounted for by the pressure alone, p. 31. It seems a question in part of the air dissolving in the carbon dioxide and in part of the carbon dioxide dissolving in the air.

"Arrhenius tried to picture the effect of a change in the proportion of carbon dioxide in the atmosphere on the surface temperature of the earth. The temperature of the earth's surface was assumed to be in equilibrium with that of the atmosphere; if, by any increase in the amount of carbon dioxide, the atmosphere retained more heat than before, it would radiate more heat to the surface of the earth. The surface temperature would then rise until equilibrium between the two occurred. The rise was assumed to be governed by the radiation law, and hence it was estimated that if the carbon dioxide is increased 2.5-3.0 times its present value, the temperature in the Arctic regions would rise 8°-9° and would produce a climate as mild as that of the Eocene Period; a decrease of 0.55 to 0.62 times its present value would cause a fall of 4°-5° and produce a glacial period. Frech and C. F. Tolman support Arrhenius' views. Kayser, Abbott, and Fowle hold that the carbon dioxide in the atmosphere cannot absorb more than sixteen percent of the terrestrial radiations; that variations in its amount are of small effect; and that the proportion of water vapor in the atmosphere is so large as to make the climatic significance [of carbon dioxide] negligible. The principal absorbent of terrestrial radiation is water vapor," p. 37.

In some cases stalagmites grow very rapidly. "The San Filippo spring (Tuscany) is said to deposit lime at the rate of twelve inches a month, and the spring has formed a bed of limestone rock 250 feet thick, 1.5 miles long and 0.33 miles wide. The building stone called travertine (Tiberstone) is probably a limestone deposited from a mineral spring," p. 81.

"Quartz which has been formed above 575° can be distinguished from quartz which has never reached that temperature. At ordinary temperature all quartz is α-quartz, but if at any time in its history a particular piece of quartz has passed the inversion point and has been heated above 575° it bears ever afterwards marks potentially present which on proper treatment can be made to appear just as an exposed photographic plate can be distinguished at once from an unexposed plate on immersion in a proper developer, although both plates may be identical in appearance before development. Wright and Larsen go further and say that quartz can be used as a geological thermometer, because if at any time quartz has been heated above 575°, this fact is recorded in its structure by the corrosion figures. Hence, also, quartz in any rock must have formed below 870°, and its peculiarities indicate whether it was crystallized above or below 575°," p. 247.

Pliny refers to a rare and costly cloth, the cremation cloth of kings. He thought that it was of vegetable origin, and gave an imaginary description of its growth in the deserts of India. Plutarch, in the first century of our era, said that asbestos was used in ancient times for making the wicks of the lamps used by the vestal virgins. In the thirteenth century, Marco Polo mentioned "an indestructible cloth made by the Tartars which was said to be made from the skin of the salamander, supposed to live in fire, but which was found to be woven from a fibrous mineral called amicanto. The knowledge of asbestos possessed by the ancients appears to have been forgotten. Apart from a few isolated cases, the industrial applications of asbestos did not attract serious attention until towards the middle of the nineteenth century," p. 425.

"Numerous observers have demonstrated the decomposition of felspar, mica, and related minerals by the action of water, and particularly water charged with carbon dioxide. Headden, for instance, said that water holding carbon dioxide in solution is nearly nine times as active as distilled water when in contact with felspar. Water can work its way into the body of granite rocks through pores and cleavage cracks; for, according to van Hise, granite rocks have a porosity of 0.2-0.5 percent. According to Bischof, one of the springs in the vicinity of Lake Leach (Germany) discharged nearly 176,000 lbs. of water carrying 0.13 percent of sodium carbonate in 24 hrs.; assuming that the sodium in felspar is converted into soluble sodium carbonate, this would represent the decomposition of nearly 18,000 lbs. of soda-felspar per annum. A few centuries would thus suffice to decompose enormous masses of granite rock. It does seem curious to find that a dilute solution of carbon dioxide has sufficient chemical strength to decompose a combination like felspar which is fairly resistant to the most powerful mineral acids; but H. Rose pointed out, in 1842, that the enormous quantities of carbonic acid which are brought into contact with the rock make up for its deficiency in chemical strength. According to L. von Struve and H. Müller, carbon dioxide under compression is more active than it is at ordinary pressures. A. Stahl considers that the clay deposits at Passau, Mederschlesien, and Odenwald have been formed from gneiss rocks by the action of the carbon dioxide. The china clay at Auvergne (France) is supposed to have been formed in this way; W. S. Bayley found that the china clay in the Piedmont Plateau, North Carolina, gradually merges downwards into felspar. The effect of carbonated waters can be easily overestimated, in contrast with the action of organic acids which are probably more powerful than carbonic acid. Ginsberg, however, claims that the formation of china clay by the action of organic acids in natural waters has not been demonstrated. H. Stremme considers that the efficiency of all the different weathering agents is really due to the chemical activity of aqueous solutions of carbonic acid—cold or hot; and K. Endell has shown that the acidity of moor-waters is largely due to the carbonic acid they contain," p. 469.

"The remarkable effects of gum and other mucilages in enhancing the plasticity of clay has been utilized by potters for an indefinitely long time. In 1903 E. G. Acheson patented the use of aqueous solutions of the tannins and gallotannins, *e.g.* decoctions of oak-bark, etc.; and in 1918 G. Keppler, and A. Sprangenberg patented the use of decoctions of humic acid, peat, etc. These plasticizing agents probably act indirectly by adsorption. The clay particles adsorb the organic colloid, and, judging by results, this probably augments the surface attraction between the particles and the surrounding liquid. The plasticity of china clays, practically free from organic matter, shows that adsorbed organic colloids are not always the source of their plasticity. Clays which have been sodden with ground waters rich in organic matter are usually highly plastic; and those clays which can be shown geologically to have been deposited in swamps and bogs, or which have been in contact with such waters, are usually very plastic unless other metamorphic changes have occurred. Many such clays, however, are not plastic when freshly dug, but they become plastic during weathering. When first mined some of the clays are hard, but if they be moistened and exposed to sunshine and frost they disintegrate more or less quickly and crumble to fine-grained plastic clays. Clays which are allowed to stand for a long time in contact with moisture become more plastic, or, as the workmen express it, more "buttery." Clays which have been boiled with water also become more plastic. Clays prepared by fast processes—filter-press—are not so "buttery" as when prepared by a slower process—slip-kiln. China clays prepared by the elaborate, apparently primitive Cornish process—by slow sedimentation and slip-kiln—are more plastic than when the process of dewatering the clay is accelerated by filter-press. There is thus an intimate connection between the plasticity of a clay and its past history with respect to water. All this looks as if the clay in contact with water is being hydrated to form a colloidal gel," p. 490.

"The ancient writers attributed the discovery of the art of making glass to the Phoenicians, but excavations in Egyptian tombs have shown that the Egyptians must have been adept glass-makers long before the Phoenicians practiced the art. This indicates that the Phoenicians were probably distributors of Egyptian glass before their own factories were established at Sidon. In the work cited above, Pliny said that glass was made in Italy, and in the Gallic and Spanish provinces, by fusing sand with three times its weight of nitre; and he added that in India rock-crystal was used in place of sand. Bases other than the alkalies are needed to make the glass resist rapid attack by moisture. These might have been added deliberately, or brought in as impurities with the sand or alkalies," p. 520.

"Representations of these processes of glass-making are depicted on the walls of the tombs of Ben-Hassam near Thebus, 3000-1700 B.C. These tombs also contain vessels, etc., showing that the artisans were not only acquainted with the making and working of glass, but also with the coloring and cutting of glass in imitation of the precious stones. F. M. de Rozière also found samples of colored glass in early Egyptian tombs. W. M. F. Petrie collected at Tell-el-Amarna specimens illustrating all stages of the process of glass-making about 1400 B.C. F. Rathgen gave analyses of antique Babylonian glass. Theophrastus, about 300 B.C., mentioned the coloration of glass by copper; and in his *Clouds* Aristophanes referred to a glass lens used as a burning glass. From Cicero, it would appear that glass from Egypt was greatly prized by the Romans; so much so that when Augustus subdued Egypt, 29 B.C., a portion of the Egyptian tribute was ordered to be paid in glass. At the time of Tiberius, Egyptian workmen were imported to Rome, and Roman glass rivalling that from Egypt was soon obtained. Works were also established in Italy, France, and Spain at an early date. In the second century, H. Philo, in his *De legatione ad Caicum Caligulum*, alluded to the use of translucent stones as windows in the halls and chambers of the emperor's palace, and in the fourth century, L. C. Lactantius, in his *De opificio Dei*, mentioned the use of glass itself for windows. It is therefore probable that about the third century glass was employed in the construction of windows; but, according to L. Dutens, the excavations of Pompeii, near Naples, show that at that time *les salles de bain étaient garnies de fenêtres en verre aussi belles que les nôtres.* After the fall of the Roman Empire the manufacture of glass was taken up in Byzantium, where it flourished for about five centuries. The fall of the Eastern Empire was attended by the migration of the glass-makers to other parts of Europe. Many were attracted to the Venetian Republic, and the Venetian glass became famous throughout the civilized world.

"In the early Middle Ages, glass-making was taken up in Germany: and in his *De re metallica* (Basiliae, 1546), G. Agricola gave a drawing of a glass furnace; and shortly afterwards H. Mathesius, in his *Sarepta* (Nürnberg, 1562), described the practice employed in Venice, Germany, and Bohemia. A. Neri published a number of recipes in 1612, and some years afterwards this work was elaborated by J. Kunckel.

"The factories in different localities acquired fame for some peculiarity in manufacture; the Bohemian manufacturers, for example, excelled in the production of colorless glass rivalling that from Venice. The manufacture of glass in Bohemia suffered a relapse owing to the heavy import duties levied against it, and the inducements held out to Bohemian workmen by foreign countries. Both the Venetian and Bohemian glass industries were revived in more recent years. The manufacture of the better types of glass in France commenced in the eighteenth century in factories erected at Paris and at St. Gobain. The latter is now famous for the manufacture of plate-glass. According to H. J. Powell, it is possible that during the Roman occupation a few beads, small cups, and bottles were made in England; but the resemblance of the scattered vessels and fragments of vessels to those found elsewhere makes it probable that there were only a few centres of glass manufacture in the Roman empire, and that the vessels were distributed from these to various parts. Glass was manufactured in England in the thirteenth century, for the industry was in existence at Chiddingfold, Surrey, in 1226. The south-eastern counties—Surrey and Sussex in particular—were favorite spots for the native glass-makers from the thirteenth to the sixteenth centuries. Glass was manufactured in Russia in the seventeenth century; and, in the United States, near the beginning of the nineteenth century.

"Theophilus, in the latter half of the eleventh century, related that, in Italy, flint glass was used for imitating gem-stones, and added that the Jews were engaged in the manufacture of these imitations. Towards the end of the eighteenth century, J. Strasser, of Vienna, was famous for his skill in this work. He made a flint glass very rich in lead, and of high refractive power and sp.gr., which was called *strass,* and which was tinted with the necessary coloring oxides— e.g. 0.8 percent of chromic oxide to imitate the emerald; a mixture with 0.8 percent of manganese oxide, 0.5 cobalt oxide, and 0.2 gold purple, to imitate the amethyst," p. 520.

"The early observers included mica in the same class as gypsum, which can also be split into thin flakes. It was afterwards noticed that, unlike talc and gypsum, the cleavage plates of mica are highly elastic, and not pliable. Pliny, in his *Historia naturalis* has a description of a mineral, *lapis specularis,* which applies very well to mica. The scales of this mineral were strewn over the *circus maximus* at the celebration of games with the object of producing a sparkling whiteness. This shows that a mica schist furnished the material employed; and Pliny's hammochrysos was probably a sand containing golden-colored scales of a biotitic mica. The Hindus appear to have used mica for decoration and other purposes, and they considered it to be endowed with extraordinary properties. Mica has also been found in the graves of prehistoric American races, east of the Mississippi, in localities where the mineral does not occur.

"The term *mica* is not likely to have been derived from the Latin *mica,* a crumb, or grain, but rather from the Latin *micare,* signifying, like the German *Glimmer,* to shine. In mediaeval times, scaly mica was called cat-silver, or cat-gold—Katzengold, or Katzensilber; *or des chats,* or *argent des chats.*Thus G. Agricola spoke of *Ammochrysos, Mica, Glimmer* or *Katzensilber.* A. B. de Boodt and J. G. Wallerius described several varieties. A. G. Werner, and A. Estner definitely adopted the term *Glimmer,* and described many varieties. No great progress could be made in the classification of the micas until they had been distinguished from one another by chemical analysis, and optical measurements," p.604.

"Muscovite is a pyrogenetic mineral which occurs as a primary constituent in deep-seated igneous rocks rich in alumina and potash, and poor in iron and magnesia. It is common in granites, syenites, and pegmatites. From its water-content muscovite was probably formed in these rocks under pressure. It does not occur as a primary constituent in recent lavas and their glassy magmas. Muscovite is common as an alteration product of many minerals—andalusite, cyanite, topaz, felspar, nephelite, spodumene, scapolite, etc. As a secondary mineral it is often called sericite. Paragonite is one of the rarer varieties; it occurs in crystalline schists, but does not occur as a pyrogenetic mineral. Lepidolite occurs in granite and pegmatite where it may form violet or lilac-colored crystals associated with muscovite. It sometimes occurs as a secondary product after muscovite, when it occurs as margins on the plates of muscovite. Cryophillite similarly occurs on plates of leipdolite," p. 609.

"The most important use of mica is in the electrical industry as an insulator. It is one of the best insulators because of its resistance to puncture, pre-resisting qualities, impermeability to moisture, toughness, elasticity, and flexibility; and its cleavage into thin sheets. It is largely used for insulating the segments of commutators, armature wires and bars, etc. Scrap mica is made into sheets, plates, and boards by means of a suitable bonding agent—say, shellac—and under the commercial name *micanite*, is used for making washers, etc., for insulating lamp-sockets, fuse-blocks, cut-out boxes, etc. Sheet mica is used for lanterns and windows where glass does not withstand the shocks and vibrations. It is also used in place of glass where abrupt changes of temprature would be liable to crack glass—*e.g.* fire-screens, stove windows, lamp-chimneys, and some miners' lamps. Special sparking plugs for aeroplanes, etc., are built up from sheet mica. It is employed as a heat insulator in the lagging of steam-pipes, boilers, etc. It is used as a sounding-diaphragm in telephones, gramophones, etc. It is used as an absorbent for nitroglycerol and as a heavy lubricant. Mica is used in making wall-paper pigments; and various ornamental purposes—a mixture of gum arabic and ground white mica makes the so-called *silver ink;* and it is employed for inlaying buttons, in making lustrous hair-powder, and in making the bronze-like colors which bear the name *brocades, crystal colors, mica-bronzes,* etc., and in making frosted effects in decoration," p. 620.

"The water in zeolites possesses the property of mobility to a high degree whilst the silicate space-lattice must be considered as relatively rigid. The water molecules entering into the mesh cavities of this lattice will tend, according to their thermal pressure, to become uniformly distributed; on the other hand, the silicate molecules (or portions thereof) in the crystal lattice will tend to hold by attraction the water molecules, or a portion thereof, in position in entire conformity with the symmetry of the latice. Both tendencies can be simultaneously satisfied only if the number of water molecules is a complete multiple of the number of silicate molecules, for only under these conditions can the water molcules arrange themselves in identical formation round each of the other molecules of the silicate lattice. It is only exceptionally favorable mixtures such as these that give the straight line in the dehydration curve. All other mixtures correspond to points on the irregular curves. The zeolites are therefore considered to be solid solutions, but it is an open question whether the water in this solution reacts with the solvent, *i.e.* forms an intimate compound with the silicate, or whether it enters the lattice as a molecule dissociated into its atoms, or into ions.

Wilder D. Bancroft

Wire-Drawing and the Cold-Working of Steel. *By A. T. Adam. 26 × 19 cm; pp. 212. London: H. F. and G. Witherby. Price: 40 shillings.* We learn from Mr. Adam's preface to this book that since the publication in 1891 of Mr. Bucknall Smith's book on Wire, no text-book dealing exclusively with Wire and allied products of cold-working processes has appeared. The present author, who is in charge of Messrs. Brunton's research laboratory, has in the present book, written not an exhaustive treatise on the subject, but an account which aims at explaining the real nature of Wire and other cold-work products. It describes their physical properties and it shows how these depend on the treatment the material has received. The book is intended for Metallurgists and Engineers and those who are interested in the product itself, rather than in the process of manufacture. Accordingly machinery and plant are only dealt with briefly, while such matters as quality and the preliminary treatment of the material, the extent of reduction by cold-work and the relation of these matters to the properties of the finished product, have been discussed more fully.

The book opens with an introductory chapter followed by two chapters on wire-drawing, including the cold-working operation. Then follow chapters on cold-rolling and other cold-working processes, heat treatment, and two chapters on the effect of cold-work on the physical properties of metals. The important subject of the effect of heat treatment after cold-work is then dealt with, and this is followed by a discussion of the theories of plastic flow in cold-worked metals. The last two chapters are concerned with the pathological aspect of cold-working operations and the application of cold-work to non-ferrous metals and alloy steels.

We think that Mr. Adam's book will be found very acceptable. It is well printed and illustrated: the photographs and drawings are excellent, and the whole treatment of the subject is scientific. The author has made a careful study of modern metallographic research bearing on wire-drawing operations, and his treatment shows that he has understood the vital bearing of certain researches in particular, which are probably destined to have an important influence on the progress of wire manufacture. To mention only one of these, now that the majority of the common metals can be obtained in the form of single crystals, which are characterized, for the most part, by remarkable ductility and malleability, it is clear that the wire-drawing of single crystals may ere long be destined to become a commercial operation. Actually, this is already so in the case of the metal tungsten. We cannot help regretting the high price at which the book is published, for we fear that it will severely limit its circulation and accessibility. *H. C. H. Carpenter*

Der molekulare Brechungskoeffizient in der Reihe der Polymethylenverbindungen. *By Fritz Eisenlohr. 25 × 14 cm; p. 48. Berlin: Borntraeger, 1925. Price: 4.20 marks.* Although the determination of the molecular refraction $[R^L]_D$, of liquid organic compounds has been of the greatest service to the organic chemist as an adjunct in the determination of structure, the application of the method for the latter purpose is limited. A number of constitutive factors do not find definite expression in the value for $[R_L]_D$ and it is only the presence of conjugated or semicyclic double linkings and three- and four-membered rings which produce exaltations from which inferences regarding structure can be made. The underlying cause of this is the fact that the refractive index and the density vary together so that the differences between related compounds are obscured.

The expression $N_D^{20} \times M$, in which the density is not taken into account, does not possess this disadvantage (Eisenlohr and Wöhlisch: Ber. 53, 1746 (1920); it is claimed that the agreement between the observed values of this "molecular coefficient of refraction" and the calculated values is of the same order as for the value $[R_L]_D$ and a series of additive constants has been calculated..

Constitutive influences are, however, very pronounced giving "exaltations" (E) which are sometimes positive and sometimes negative. Thus, the branching of a carbon chain has a positive effect of 0.45 unit; the introduction of an ethyl group in the place of a hydrogen produces a different effect from that of a methyl group, etc.

Ring formation causes an appreciable negative exaltation, different for every type of ring and decreasing regularly from cyclopropane to cyclooctane. The effect of substitution in the benzene ring is different according to the position of the entering group, an ortho substituent giving the highest, para- the lowest exaltation. In alicyclic ring compounds a further factor has to be taken into consideration, namely cis-trans isomerism about the plane of the ring, doubtless owing to its effect on the "packing" of the molecules. The greater part of the work under review is devoted to the discussion of observations on hydrocarbons, alcohols, and ketones of the cyclohexane series.

The new method is doubtless a step forward towards the correlation of the physical properties of organic compounds with their structure. The choice of temperature (20°) and wavelength (D) appear to be arbitrary although it may be mentioned that dispersion is taken into account in the experimental portion of the work. In any case, the special value of the method would appear to lie in enabling conclusions to be drawn as to the structure of isomeric or otherwise closely related compounds, when discrepancies due to the calculated constants are eliminated. It is hoped that the systematic study of organic compounds from the point of view of their molecular refractive index will be materially extended in the near future and that Professor Eisenlohr's paper is but a forerunner of a more comprehensive work.

G. A. R. Kon

Die gasanalytische Methodik des dynamischen Stoffwechsels. *By Wilhelm Klein and Maria Steuber. 25 × 18 cm. Leipzig: G. Thieme. Price: 5.40 marks.* This small monograph of 100 pages deals with the various forms of apparatus used in determining the gaseous exchanges consequent upon physiological experiments, or upon pathological conditions met with in clinical practice.

The various methods used in physiological experiments for the measurement of oxygen uptake and carbon dioxide output are described with much practical detail, and the text is well illustrated with drawings of apparatus. Specimen calculations are appended as an aid to those unfamiliar with the technique. Amongst the methods described may be mentioned those of Pattendorf-Tigerstadt and Zuntz-Geppert.

The section devoted to apparatus for clinical use is much shorter, describing only the Benedikt and Krogh methods.

The gas analysis apparatus which is essential to experiments on gaseous exchange is described at length with working details.

Many useful hints are given on such practical points as the cleaning of mercury and the sampling and storage of gases, and a number of tables for the simplification of calculation are appended.

The order in which the matter is presented is good, but the division into sections is far from satisfactory. Such sections as "The Solubility of Gases in Liquids" and "The Sampling and Storage of Gases" are given equal importance with "Methods of Gaseous Exchange," which occupies over 70% of the total book, with the result that quite important subjects are almost lost under small sub-headings. A further improvement which may be suggested is that the references should be collected together and printed as an appendix, instead of being scattered throughout the book as foot-notes.

In conclusion it may be said that the book is written in easy straight-forward German, so that it may be used as a book for laboratory reference by those who do not read German fluently.

W. K. Slater

Molekulargrössen von Elektrolyten in nichtwässerigen Lösungsmitteln. *By Paul Walden. 23 × 15 cm; pp. xi+350. Dresden and Leipzig: Theodor Steinkopff, 1923 Price: paper $2.25, cloth $2.58.* The subject is presented under five headings: general remarks on molecules and polymerization; recognition and determination of molecular weights or of degree of polymerization of homogeneous liquids; molecular weights or degree of polymerisation of dissolved substances; the molecular weights of dissolved electrolytes by the osmotic methods; general results of molecular weight determinations of salts, acids, and bases in non-aqueous solutions.

On p. 18 Walden quotes from Arrhenius. "If a star consisted of hydrogen alone and, like our sun, lost two gram calories per gram of its mass every year, it could keep that up for eighty-seven billion years in case the heat radiated were compensated by the condensation of hydrogen into heavy atoms."

Walden considers, p. 41, that the change of color of cupric bromide solutions from blue to dark-brown with increasing concentration is due to the increasing formation of polymerised cupric bromide $(CuBr_2)_x$. It is difficult to see how this is consistent with the assumption of hundred percent dissociation; but of course Walden does not believe in hundred percent dissociation.

Ramsay's surface tension experiments make the degree of polymerisation of water at 100° about 1.5 while Walden calculates it as nearly 2.0, p. 56. On either assumption there is a considerable degree of association and this must have its effect on boiling-point determinations. One would rather like to see a series run at about 200° which would only mean fifteen atmospheres or so. On p. 71, Walden quotes Küster to the effect that solid naphthalene and solid naphthol are both bimolecular.

Walden considers molecular weight determinations of 25000 for starch and 5000 for ferric oxide as not unreasonable, p. 84. He quotes results of 4500 for tetra-ethyl ammonium nitrate in chloroform, p. 198, and says that this substance is in true solution; but there must be some error about this.

"The constitutive factor of the electrolyte, which often does not show at all in aqueous solution, becomes of great importance for the strong binary salts in non-aqueous solutions. The non-aqueous solutions furnish the proof that the acids are electrolytes of a different type from the salts because the acids, like hydrochloric acid, trichloracetic acid, and tribromacetic acid, which are as highly dissociated in water as the binary salts, are practically not dissociated at all in solvents in which the salts are ninety percent dissociated," p. 311.

The associating power of a solvent varies inversely as the dielectric constant, the dissolved salts being polymerized more strongly, the lower the dielectric constant is. Conversely, the dissociating power of the solvent is greater, the higher its dielectric constant," p. 312.

"Through variation of the solvent the same salt of the type of a binary iodide, MI, can be obtained in all stages of polymerization or dissociation at the same concentration and temperature. At the same temperature and concentration we can therefore obtain a given salt in the form of highly polymerized molecules with an apparent molecular weight of infinity, or in the form of a molecule dissociated almost completely into free ions. We get this extraordinary plasticity of the apparently so firmly knitted salt molecule not by making use of special energy factors, but simply by dissolving it once in a so-called indifferent solvent, and the next time in a strongly ionizing solvent. From both solvents we recover the unchanged salt on crystallization," p. 312.

The author prides himself on the treatment being non-critical; but one cannot share this enthusiasm.

Wilder D. Bancroft

Crystals and the Fine-Structure of Matter. *By Friedrich Rinne. Translated by Walter S. Stiles. 23 × 15 cm; pp. ix+195. New York: E. P. Dutton and Company. Price: $4.20.* "Crystals are proving themselves more and more the ideal substances of physics and chemistry. Even before the last great discoveries in this branch of knowledge the late Woldemar Voigt, Professor of Theoretical Physics at Göttingen, who had a unique knowledge of this subject, drew attention to the exceptional regularity of the crystalline parts of matter in a fine simile, which is quoted below:

"Imagine a couple of hundred picked violin players in a large room, all playing the same piece of music on faultless instruments, but beginning simultaneously at widely different places, and starting afresh each time they reach the end. The finest ear would be unable to recognise the piece actually played in this uniform medley of sound. Now such music is presented to us by the molecules of gaseous, liquid, and ordinary solid bodies. A crystal, on the other hand, corresponds to the orchestra described above when it is guided as a whole by one able conductor, so that all eyes hang on his slightest gesture, and all hands play the same bar. In this way the melody and rhythm of the piece presented became completely effective, the number of the performers not hindering but intensifying the result."

"This picture makes it clear how crystals can present a large series of phenomena which are absent in other bodies, and that, in them, certain characteristics are developed in wonderful variety and elegance, which elsewhere occur only as monotonous mean values," p. 2.

"I introduce the expression fine-structure-study, or leptology, because the customary term stereochemistry does not cover completely the field of the inquiry intended. In stereochemistry we study the form and arrangement of the particles comprising various substances in order to explain thereby their chemical properties. Alongside this science, another has arisen, which may justly be termed stereophysics, and this also is concerned with the constitution and association of the particles of matter, dealing especially with their movements and physical properties (e. g. crystal optics). Finally, a third allied subject is included, namely, crystal structure, or the study of the fine-structure of crystalline bodies from the point of view of their geometrical relations.

"Thus from the trunk of Greek Atomic Theory, which is more than two thousand years old, three branches of knowledge have sprung forth and blossomed—stereochemistry, stereophysics, and crystal structure. Their intimate relations to one another justify a name to include them all. If now the particles of matter, the electrons, atoms, ions, and molecules which constitute gases, liquids, and crystals are termed collectively fine-structure-particles or leptons (from λεπτος, fine, delicate), the name suggested above, fine-structure-study or leptology indicates precisely the end in view," p. 5.

"Substances built up of flakes, which lie with all their fibre axes or flake normals parallel, but otherwise indifferently, give on the passage of X-rays perpendicular to this direction and X-ray effect similar to that of a crystal plate which is rotated about an axis passing through it. The series of reflexions, one after the other, produced by the latter, as a result of the rotation, are shown by the pack of fibres or flakes simultaneously. All fibres or flakes, the structure planes of which satisfy the equation $n\lambda—2\pi \sin \alpha$ give rise to reflected rays. As was shown by H. Seeman and E. Schiebold, in particular for rotating plates, and M. Polanyi for fibrous substances and stretched metals, we get in this way characteristic diagrams," p. 17. On this statement of facts, X-ray photographs apparently do not show whether a fibrous or flaky substance is or is not crystalline.

"The idea of deriving the multiplicity of crystallographic forms from five types all mutually connected, which may be called primitive forms, has already been brought forward by G. v. Tschermak, and followed in his teaching," p. 28. The five primitive forms are called: pedion, pinacoid, sphenoid, doma, prisma.

"The chief difference in the construction of crystalline bodies and the individuals of amorphous substances lies in the restriction of the rhythm. In the fine-structure of crystals, owing to the fact that each structural unit is joined to its neighbours, this rhythm exhibits a three-dimensional periodicity. Such space-lattice structure is clearly only possible when the repetition is according to the numbers 2, 3, 4, and 6, or with no repetition at all. Pentad, septad, and compound axes of higher period are here theoretically excluded, nor are they found in practice," p. 49.

"The change of physical properties with direction is very obvious in crystals showing cleavage. Thus for rock-salt there are three directions, perpendicular to the cube surfaces, in which the cohesion of the crystal is a minimum. The resistance to splitting in these directions is only one-third of that in the direction of the cube diagonal. The cleavage planes are, therefore, regularly oriented surfaces of maximum brittleness. In like manner, many crystals show particular planes of maximum plasticity. These are surfaces in which internal displacements may easily occur; with ice they arise as planes parallel to the surface of the ice floe. Hardness is also a directional property in crystalline materials. The resistance to disrupture, which shows itself as hardness, is often different in different directions of the crystal; thus it is a familiar fact to diamond workers that the cube surfaces of the gem are more difficult to prepare by polishing than the octahedron surfaces. Garnet, too, is harder on the cube surfaces than on the octahedron and rhombic dodecahedron, according to the researches of P. J. Holmquist on polishing. Even on the same surface of a crystal the hardness, as measured by scratching, varies with the orientation of the scratch made by the test needle. Cyanite is a classical example of this," p. 55.

"The great disperseness of gases is enormously diminished on crystallisation: in liquids, too, in general, the same thing occurs. In this connection some figures for sodium and the diamond, as two extreme types, will be of interest to the reader.

Number of atoms sodium per c.c.		Ratio
1. Gas at boiling-point (820°C)	5.5×10^{18}	3550
2. Liquid at boiling-point	$19,500 \times 10^{18}$	
3. Liquid at solidifying-point, 97.6°C.	$24,500 \times 10^{18}$	1.03
4. Crystal at solidifying-point	$25,000 \times 10^{18}$	

"In solid sodium, with its body-centred space-lattice (only two atoms in the elementary cell) and its large a-value for the cube edge (4.3×10^{-8} cm.), we are dealing with a soft metal. The condensation from gas to fluid is considerable; that for fluid to crystal, small.

With the hard, compact diamond (eight atoms in the elementary cell, $a = 3.53 \times 10^{-8}$ cm.), a much more extensive condensation occurs on crystallisation; 1 c.c. of this gem contains 180,000 trillion carbon atoms, compared with 1.3 trillion in carbon vapour at 5500°C. Naturally, with such close packing of the particles of matter, the cohesion between them becomes enormous," p. 66.

"Considering the results already obtained in crystal leptology with a view to a physical chemical interpretation, the desired organisation into radicals is, in fact, often definitely shown in the architecture. The Braggs, as originators of fine-structural schemes, have pointed out the dumbbell-like connection of the two sulphur atoms in iron pyrites, and, in somewhat greater detail, P. Niggli has expressed the opinion that the representation of the complete crystal as a purely atomistic space-lattice complex certainly may always be carried out formally, but that many inter-connections between certain atoms forming structural groups (as P. Niggli called them) stand out clearly on a merely architectural consideration of the schemes. These structural groups I have designated geometrical radicals or leptyles in adaptation to chemical ideas. Finally, groups of a molecular nature are occasionally unmistakable in the crystal arrangement. Such leptyles occur in iron pyrites with its doublet S_2, in calcspar with the ion CO_3, and in rutile and anatase with the molecular TiO_2 complex. A fine example of leptyle grouping has been investigated by Dickinson (1922). Moreover, for organic substances with ring formation, such a fine-structural grouping must be assumed according to P. v. Groth, who formerly brought into prominence the atomistic crystal structure. As regards cyclic chains of atoms so fundamental chemically, which can with certainty be attributed to the molecules of benzene, naphthalene, and other organic substances, it is more than probable that these chains persists in crystallisation. Crystallised organic compounds will often be molecular aggregates loosely knit into space-lattices. This conception W. H. Bragg has taken as fundamental in his present researches on organic compounds," p. 90.

"The undermining of crystals may, however, take place to an extent much greater than is represented by the removal of a relatively small part of the constituents which water usually represents. The calcium aluminium hydrosilicate $CaOAl_2O_36SiO_2$ ca. 5.5 aq. of heulandite, for example, may be reduced fine-structurally to SiO_2. The entire filling of basic constituents is then removed, the result being just as though the skeleton of some siliceous plant had been prepared by burning the organic wrapping. The relict of the zeolite so obtained still shows (especially after glowing, probably under the influence of collective crystallisation) definite optical agreement with the original substance, the hard rigid pseudomorph of which it represents. If, starting from desmine zeolite, all the basic constituents are simultaneously withdrawn with hydrochloric acid, a SiO_2 optically analogous to the original desmine is obtained. Thus the same chemical substance SiO_2 appears here to have a varying structure depending on its previous history; in the one case it is a heulandite, in the other a desmine residue," p. 151.

"The space-lattice constitution of the crystal must serve as the fundamental conception in this work. In its particular fine-structural symmetry and special tectonic nature are characterised the physico-chemical connections of the particles. As a result of this, for every particular case we find at once certain indications as to the mechanics of the chemical processes in the bodies concerned, and a basis for generalisation is obtained. Since, for example, $CaCO_3$ of calc-spar, which is constructed from $Ca^{\cdot\cdot}$ and CO_3 ions in a ternary rhythm, undergoes, on heating, the well-known reaction of splitting into CaO and CO_2, it must be assumed for the fine mechanics of this process that, on account of the increased heat motions, first the geometrico-chemical radical CO_3, as a ring of three O's about a centre carbon, becomes loosened in the fine-structure. With increasing temperature these radicals, together with the calcium atoms, which are free moving groups in the material field, undergo a separation into CO_2 and O, which links up with Ca to form CaO.

"According to this, the loosening of the particles in the fine-structure is always to be regarded from the standpoint of symmetry action. Those particles of the structure, coupled together by rhythm or reflexion, participate simultaneously in the process, and since such coupling thus occurs throughout the entire crystal many million times, the process appears to us in analytical chemistry as a disontinuous change, possibly in a series of steps, if the new arrangement contains the departing component again in definite symmetry disposition, as is the case, for example, in the ignition of gypsum to the subhydrate. A practically steady variation can have its origin in complicated re-groupings of the point system, closely following on one another," p. 158.

Wilder D. Bancroft

A Text-book of Organic Chemistry. *By E. de Barry Barnett. 21 × 14 cm; pp. xii+380. Philadelphia: P. Blakiston's Son and Co., 1920. Price: $5.00.* In this general survey of the most important classes of organic compounds, the author has attempted to emphasize group reactions rather than the reactions of individual compounds, so that the number of individual substances mentioned is smaller than is generally the case. However, the group reactions are illustrated by means of specific cases in the usual way.

Although descriptions of analytical methods must necessarily be meager in a book of this type, mention might have been made of the use of the Parr bomb in determining halogens and sulfur in organic compounds, since it is extensively used.

Whether or not the arrangement of the material is the best possible one is probably a matter of personal opinion. All of the general theories (Isomerism, Stereoisomerism, etc.) are presented in the Introduction, "as they are more easily referred to when necessary". The compounds are classified in the usual way and all of the members of one class are considered together, rather than dealing with the simpler members of the various classes first and then treating the more complex substances later.

The material covered is quite up-to-date, although some things have been omitted that might well have been included. For instance:—The preparation of acetic aldehyde from acetylene and the conversion of the aldehyde into acetic acid and alcohol are discussed. No mention is made of the fact that the acetic acid thus obtained is converted into acetone by passing its vapors over hydrated lime at 485°. Bakelite is not mentioned.

Unusual features of the book for an elementary treatise are (1) a brief discussion of the available literature, (2) a list of the more important books dealing with the subject matter is placed at the end of each chapter and (3) the objections to the Kekulé formula for benzene are considered.

With regard to the index, the convenient feature of printing the main references in heavy type is not followed.

Ralph T. K. Cornwell

A Systematic Handbook of Volumetric Analysis. *By Francis Sutton. Eleventh edition. Revised by W. Lincoln Sutton and Alfred E. Johnson. 22 × 16 cm; pp. xii+629. Philadelphia: P. Blakiston's Son and Company, 1924. Price: $9.00.* The authors have endeavored in this edition to cover the volumetric methods for the analysis of ores, ferrous and non-ferrous materials, water and sewage, organic substances, urine and gas and "to describe all the operations and chemical reactions as simply as possible." Therefore, it is not surprising in a text covering so much material that some errors of omission are made, such as electrometric and conductivity titrations, benzoic acid as an alkalimetric standard, some of the better methods for aniline and phenol and most of the American advances in gas analysis apparatus.

It is surprising, however, to find in the 11th edition of a book the use of "floats" instead of the complete circling of burettes by graduation marks at major points as advocated by the U. S. Bureau of Standards and the statement that after a burette is rinsed with a solution, it "is nearly filled with the solution and a considerable amount of the liquid allowed to flow back into the bottle from which it is being filled." A few careless errors have been made such as "$2Na_2C_2O_4$ yield O_2" and the placing of a soda-lime guard tube for alkaline solutions in a vertical position.

However, this work contains a great variety of volumetric methods for all of the determinations covered and numerous references to the literature. For this reason it will undoubtedly be of value to analytical chemists as a very handy reference book. The reviewer feels, however, that the value of the book would be greatly enhanced if the authors had indicated which method they considered the best for each individual determination.

M. L. Nichols

Quantitative Analysis. *By Stephen Popoff. 20 × 14 cm; pp. xiii+342. Philadelphia: P. Blakiston's Son and Co., 1924. Price: $2.25.* The author states that his objects in writing his book are threefold: First, to incorporate in a single book, theory, laboratory instructions, problems and their explanation; second, to emphasize the law of mass action and the theory of equilibrium as applied to quantitative analysis and third, to incorporate some of the more recent advances in this field. In satisfying the first purpose, there is nothing to warrant an extra need of praise. A normal solution is defined as one which contains 1 g. of hydrogen equivalent per liter of solution.

In accomplishing his second purpose, much material is included which is generally found in texts for qualitative analysis and there are certain principles of physical chemistry not usually to be found in quantitative analysis texts, e.g., van der Waals' equation and for which the author feels it necessary to present an "excuse". In the section dealing with special topics, we find electro-analysis, food analysis, iron and steel analysis, and electrometric titrations. For laboratory practice in the first three topics, the author issues supplementary mimeographed instructions. The chapter on electrometric titration is the redeeming feature of this section. *M. L. Nichols*

The Properties of Matter. *By Basil C. McEwen. 20 × 14 cm; pp. vii+316. New York and London: Longmans, Green and Co., 1923. Price: $3.20.* "The order followed is the reverse of that adopted in most Text-books dealing with the Properties of Matter.

"Commencing with the First Law of Thermodynamics, an extension is made to the more general Principle of the Conservation of Energy, and hence to the metaphysical conception of the Identity of Energy throughout its various transformations.

"Since our knowledge of mechanical systems is, in general, more complete than that relating to other modes of energy, a logical sequence leads to the study of the Kinetic Theory of Matter, the consequences of which can be most fully developed when applied to matter in the gaseous state.

"The Properties of Gases are, therefore, next investigated from the standpoint of the Kinetic Theory, and the continuity of the gaseous and liquid states supplies the natural transition to a detailed study of liquids. The Properties of Solids are dealt with last.

"It is thought that this method of treatment is simpler, and follows a more natural sequence than is attained by commencing with a study of the Properties of Matter in the solid state—and proceeding, in the reverse order, to a consideration of Liquids and Gases," p. 5.

The chapters are entitled: the first law of thermodynamics, the kinetic theory of matter and its application to the gaseous state; isothermal and adiabatic transformations and the specific heats of gases; the elasticity of gases, and the continuity of the liquid and gaseous states; the thermal expansion, diffusion, and solubility of gases; equations of state; liquids, capillarity; solids; gravity. There are also three appendices; the Joule-Thomson effect; the theorem of LeChatelier; units and dimensions.

Wilder D. Bancroft

INDIVIDUAL THERMODYNAMIC BEHAVIORS OF IONS IN CONCENTRATED SOLUTIONS INCLUDING A DISCUSSION OF THE THERMODYNAMIC METHOD OF COMPUTING LIQUID JUNCTION POTENTIALS*

BY HERBERT S. HARNED

As a result of earlier experimental investigations[1], some tentative conclusions were reached regarding the individual activity coefficients of the ions of some simple electrolytes, and the hydrogen ion in certain chloride solutions. From the electromotive force data then available, an attempt was made to compute the individual ion activity coefficients of the hydrogen, lithium, sodium, and potassium ions in solutions of their chlorides, and the hydrogen and hydroxyl ions in solutions of chlorides. More recently, further data[2] have been obtained which complete this experimental study, and which will be assembled in this paper.

Since the difficulty in estimating liquid junction potentials is the only cause of our not being able to estimate exactly the individual activity coefficients of the ions, an analysis of the problem of liquid junction potentials will be made.

Hückel[3] has computed the individual ion activity coefficients of solutions of hydrochloric acid and sodium chloride by means of the general theory of Debye and Hückel and has found a qualitative but not quantitative agreement with our earlier conclusions. This, indeed, is to be expected since our conclusions have been considered to be but a rough approximation and not an exact solution of the problem, and since, on account of the theoretical complexity of the problem, it is not to be expected that the theory of Debye and Hückel is exact in the very concentrated solutions. In the following discussion, we shall consider these matters more fully.

(1) *Electromotive Forces of the Cells:*

$$H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o), MCl(m) \mid H_2$$

$$H_2 \mid MOH(m_o), MCl(m) \mid KCl(sat) \mid MOH(m_o) \mid H_2$$

Throughout these studies, we have employed cells containing a saturated potassium chloride solution for the purpose of reducing the liquid junction potentials as far as possible experimentally. In all cases stationary junctions were employed. These were made by having a capillary tube from one electrode compartment dip into a cup containing the other electrode solution. A mixing of the two solutions across the boundary was therefore allowed to take place. The more recent results were obtained from cells of the types

---

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] J. Am. Chem. Soc., **37**, 2460 (1915); **38**, 1986 (1916); **42**, 180 (1920).

[2] J. Am. Chem. Soc., **47**, 684, 689 (1925); Harned and Swindells: **48**, 126 (1926).

[3] Physik. Z., **26**, 93 (1925).

$$H_2 \mid HCl(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$

$$H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg.$$

All these data are compiled in Table I. The standard calomel electrode has been eliminated, and the electromotive forces corresponding to the transfer of the hydrogen or hydroxyl ions plus the liquid junction potentials have been given. At the end of the table, the values of the reference cells have been tabulated. These data come from three sources. Those denoted (1) were taken from our earlier study[1]; those denoted (2) have been recently determined; and those denoted (3) have been recently obtained in this laboratory by Dr. Swindells. Molal concentrations have been employed. All measurements were carried out at 25°. The agreement between the more recent results and those previously determined was found to be good.

TABLE I

(1) Electromotive Forces of Cells:

$$H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o),MCl(m) \mid H_2$$

$$m_o = 0.1$$

KCl		NaCl		LiCl	
m	E_H	m	E_H	m	E_H
	(1)		(1)		(3)
0.1380	0.0003	0.1867	0.0011	0.0705	0.0012
0.2775	0.0005	0.569	0.0041	0.1101	0.0017
0.560	0.0012	0.614	0.0041	0.2004	0.0021
0.848	0.0021	1.536	0.0128	0.3693	0.0041
			(2)		
1.141	0.0036	0.0959	0.0012	0.704	0.0083
1.441	0.0052	0.1779	0.0014	1.007	0.0120
3.473	0.0169	0.3456	0.0024	2.198	0.0283
	(2)				
1.341	0.0045	0.857	0.0063	3.695	0.0492
2.006	0.0082	1.707	0.0153	—	—
2.696	0.0123	2.130	0.0198	—	—
3.346	0.0161	2.599	0.0246	—	—
—	—	2.978	0.0285	—	—
—	—	3.424	0.0328	—	—

---

[1] Harned: J. Am. Chem. Soc., 37, 2460 (1915).

$m_o = 0.01$

KCl		NaCl		LiCl	
m	E_H	m	E_H	m	E_H
	(2)		(2)		(3)
0.02	−0.0003	0.02	−0.0002	0.0077	−0.0003
0.05	−0.0008	0.05	−0.0007	0.0103	−0.0003
0.1	−0.0015	0.1	−0.0005	0.0194	0.0001
0.2	−0.0021	0.2	0.0000	0.0422	0.0005
0.5	−0.0015	0.5	0.0014	0.0727	0.0011
1.	0.0016	1.	0.0058	0.1989	0.0020
2.	0.0071	2.	0.0152	0.402	0.0035
3.	0.0126	3.	0.0254	0.699	0.0072
—	—	—	—	1.004	0.0104
—	—	—	—	2.189	0.0260
—	—	—	—	3.989	0.0526

(2) Electromotive Forces of Cells:

H_2 | MOH(m_o),MCl(m) | KCl(sat) | MOH(m_o) | H_2

$m_o = 0.1$

KOH,KCl		NaOH,NaCl		LiOH,LiCl	
m	E_{OH}	m	E_{OH}	m	E_{OH}
	(1)		(1)		(3)
0.262	−0.0013	0.472	−0.0044	0.1512	−0.0051
0.527	−0.0015	0.943	−0.0071	0.2908	−0.0082
1.357	−0.0009	1.445	−0.0094	0.432	−0.0108
2.167	0.0004	1.946	−0.0107	1.071	−0 0201
3.280	0.0044	2.458	−0.0120	1.709	−0.0284
	(2)		(2)		
0.1285	−0.0004	0.1704	−0.0029	2.675	−0.0384
0.2645	−0.0009	0.336	−0.0041	3.521	−0.0461
0.647	−0.0016	0.841	−0.0075	—	—
—	—	1.696	−0.0108	—	—
—	—	2 500	−0.0135	—	—
—	—	4.14	−0.0149	—	—

$m_o = 0.01$

KOH,KCl		NaOH,NaCl		LiOH,LiCl	
m	E_{OH}	m	E_{OH}	m	E_{OH}
	(2)		(2)		(3)
0.0496	−0.0036	0.0621	−0.0054	0.0078	−0.0005
0.1026	−0.0048	0.1462	−0.0076	0.0221	−0.0020
0.1928	−0.0067	0.302	−0.0094	0.0423	−0.0036
0.4889	−0.0081	0.362	−0.0096	0.0864	−0.0070
1.051	−0.0081	0.572	−0.0117	0.844	−0.0217
1.830	−0.0071	0.853	−0.0133	1.854	−0.0360
2.446	−0.0050	1.288	−0.0157	2.746	−0.0469
—	—	1.724	−0.0172	3.810	−0.0573
—	—	2.835	−0.0202	—	—
—	—	3.575	−0.0217	—	—

(3) Reference Cells:

H_2 | $HCl(0.1)$ | $KCl(sat)$ | Hg_2Cl_2 | Hg; $E = 0.3102$
H_2 | $HCl(0.01)$ | " ; $E = 0.3679$
H_2 | $KOH(0.1)$ | " ; $E = 1.0040$
H_2 | $KOH(0.01)$ | " ; $E = 0.9491$
H_2 | $NaOH(0.1)$ | " ; $E = 1.0031$
H_2 | $NaOH(0.01)$ | " ; $E = 0.9485$
H_2 | $LiOH(0.1)$ | " ; $E = 1.0028$
H_2 | $LiOH(0.01)$ | " ; $E = 0.9483$

(2) *Discussion of Experimental Results*

According to the dissociation theory of Arrhenius and van't Hoff, it was assumed that the thermodynamic coefficients of the two ions of a uniunivalent electrolyte in a given solution were identical. Both ions were assumed to have the same van't Hoff coefficient as long as this quantity was taken as a measurement of the degree of dissociation. More recently, many investigators have come to the conclusion that the thermodynamic coefficients such as the activity, osmotic, or van't Hoff coefficients[1] are not the same for the two ions of a given electrolyte but that each ion is characterized by an individual value for this thermodynamic property.

As a first step towards evaluating the individual ion activity coefficients of highly polar electrolytes, we have made the very simple assumption that at a given concentration the relative partial free energies of the ions of the alkaline chlorides are additive. This assumption was first adopted by MacInnes for moderately dilute solutions. MacInnes[2] also assumed that in a solution of potassium chloride the activity coefficients of the potassium and chloride ions are equal. On account of the complicated nature of this problem, and the consideration of the numerous factors which may influence activity coefficients, these too simple assumptions are not to be expected to be more than a first rough approximation when applied to the very concentrated solutions. Our first step, however, in the following discussion will be to apply these assumptions to the completed data in hand.

If $\overline{F}_1$, a_1, and $\overline{F}_2$, a_2 are the relative partial free energies and activities of an electrolyte or an ion in two solutions of concentrations m_1 and m_2, respectively, then

$$\overline{F}_2 - \overline{F}_1 = RT \ln a_2/a_1 \qquad (1)$$

The electromotive force of a concentration cell, $E_1 - E_2$, or ΔE at constant temperature and pressure is given by

$$NF\Delta E = NF(E_1 - E_2) = \overline{F}_2 - \overline{F}_1 = (-\Delta F) \qquad (2)$$

From these two equations, it is seen that a change in partial free energy of an ion or electrolyte in passing from one concentration to another is proportional to the electromotive force of a concentration cell containing the electrolyte at these two concentrations, which in turn is proportional to the logarithm of the ratio of the activities at the two concentrations. With these relations in mind, we shall state the above postulates as follows:

---

[1] For definitions of these quantities, see Taylor: "Treatise on Physical Chemistry", pp. 728, 753, 754 (1924).

[2] J. Am. Chem. Soc., 41, 1086 (1919).

(1) The relative partial free energies, or electromotive forces of the ions of potassium, sodium, and lithium chlorides in aqueous solution at a given concentration and referred to a given concentration are additive,

(2) E_K equals E_{Cl} (referred to a given concentration) in an aqueous potassium chloride solution of a given strength, and follow the consequences of their adoption.

In this discussion, the nomenclature and conventions regarding the signs of electromotive forces employed by Lewis and Randall[1] will be adopted. Let us first consider the cells:

Type (1): $H_2 \mid HCl(m_o) \mid Hg_2Cl_2 \mid Hg$; ($E'$ has a positive value)

Type (2): $H_2 \mid HCl(m_o),MCl(m) \mid Hg_2Cl_2 \mid Hg$; ($E''$ has a less positive value than E'). If the second be subtracted from the first, we obtain

Type (3): $Hg \mid Hg_2Cl_2 \mid HCl(m_o),MCl(m) \mid H_2 \mid HCl(m_o) \mid Hg_2Cl_2 \mid Hg$; ($E_{HCl}$ has a positive value). The equation which relates E_{HCl} to the activities is at 25°

$$E_{HCl} = 0.05915 \log \frac{a_{H(S)}\, a_{Cl(S)}}{a_{H(m_o)} a_{Cl(m_o)}}$$

$$E_H + E_{Cl} = 0.05915 \log \frac{a_{H(S)}}{a_{H(m_o)}} + 0.05915 \log \frac{a_{Cl(S)}}{a_{Cl(m_o)}} \qquad (3)$$

where a_H etc. are the activities of the ions denoted by subscript, (s) refers to the solution containing the salt, and E_H and E_{Cl} are the electromotive forces corresponding to the relative partial free energies of the hydrogen and chloride ions, respectively. E_H would be the electromotive forces of the cells

Type (4): $H_2 \mid HCl(m_o) \mid HCl(m_o),MCl(m) \mid H_2$

where the liquid junction potential has been eliminated by some means (indicated by italic letter E). The electromotive forces of cells of this type, we shall denote $E_{H(MCl)}$. The nearest approach which has been made to an experimental realization of such cells has been obtained by interposing a saturated potassium chloride solution between the two electrode solutions. Thus, we obtain the cells

Type (5): $H_2 \mid HCl(m_o) \mid KCl(sat) \mid HCl(m_o),MCl(m) \mid H_2$

and, the smaller the difference between the two liquid junction potentials, the nearer its electromotive force will be to the E_H. Their electromotive forces we denote $E_{H(s)}$ where the (s) refers to the saturated potassium chloride.

Our procedure will be as follows. We shall first calculate E_{Cl} according to postulate (2). Values of E_{KCl} have been given in another place[2] which when divided by 2 give the values of E_K or E_{Cl} in Table II. By subtracting these from the revised values of E_{HCl} obtained at round concentrations from the plots of electromotive computed from the results in Table III of a recent paper[1] we obtain $E_{H(MCl)}$ which we compare with the values of $E_{H(s)}$ read off curves of the results in Table I of this paper. This has been done for the cells containing acid at concentrations 0.01 and 0.1 M and potassium, sodium, and lithium chlorides at concentrations (m). The results are given in Part I, Table II.

---

[1] "Thermodynamics", (1923).

[2] J. Am. Chem. Soc. 47, 930 (1925).

In Part II, the data of the hydroxide cell electromotive forces have been compiled in a similar manner. In this case, for sake of convenience, we consider the cells

Type (6): $H_2 \mid MOH(m_o),MCl(m) \mid M_xHg \mid MOH(m_o) \mid H_2$; ($E_{MOH}$ has a positive value) where M may be either lithium, sodium, or potassium. The electromotive forces of these cells are given by

$$E_{MOH} = 0.05915 \log \frac{a_{M(s)}\, a_{OH(s)}\, a_{H_2O(m_o)}}{a_{M(m_o)}\, a_{OH(m_o)}\, a_{H_2O(s)}}$$

$$E_M + E_{OH} = 0.05915 \log \frac{a_{M(s)}}{a_{M(m_o)}} + 0.05915 \log \frac{a_{OH(s)}\, a_{H_2O(m_o)}}{a_{OH(m_o)} a_{H_2O(s)}} \qquad (4)$$

E_M for the sodium and lithium ions have been calculated by subtracting E_{Cl} from E_{NaCl} and E_{LiCl} and the values are given in second and third columns in Part II, Table II. E_{NaCl} were obtained from the data compiled by Harned[2] and E_{LiCl} from the data of Harned and Swindells[3]. If E_M be subtracted from E_{MOH}, we obtain E_{OH} which corresponds to the cells

Type (7): $H_2 \mid MOH(m_o),MCl(m) \mid MOH(m_o) \mid H_2$

and the cell reaction

$$OH^-(s) + H_2O(m_o) = OH^-(m_o) + H_2O(s).$$

Thus, if E_{OH} is negative, $a_{OH(m_o)}$ will be greater than $a_{OH(s)}$ and the reaction will tend to take place from right to left. The values of E_{OH} calculated by the above method in the cases of the three chlorides are given in the table and there compared with the values of $E_{OH(s)}$, or the electromotive forces of the cells

Type (8): $H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid MOH(m_o) \mid H_2$

These latter results were read off plots of the results in Table I.

In Fig. 1, the values of E_H and E_{OH} of the solutions containing 0.1 M acid and hydroxide calculated by means of our postulates are plotted against m. $E_{H(s)}$ and $E_{OH(s)}$ are similarly plotted and represented by the dashed lines. The maximum difference between the two sets of curves occurs at 3M lithium chloride in the acid solution and amounts to 5 millivolts. In general, the curves separate rapidly upon the first addition of salt and then become approximately parallel with a slowly widening difference. E_{OH} coincides with

---

[1] J. Am. Chem. Soc., **48**, 326 (1926).

[2] J. Am. Chem. Soc., **47**, 930 (1925), Table III, E_3 in Part I and II, B.

[3] J. Am. Chem. Soc., **48**, 126 (1926).

TABLE II

Comparison of E_H and E_{OH} to $E_{H(s)}$ and $E_{OH(s)}$

Part I. The Acid System

$m_o = 0.1$

		KCl		NaCl		LiCl	
m + 0.1	$E_K = E_{Cl}$	E_H	$E_{H(s)}$	E_H	$E_{H(s)}$	E_H	$E_{H(s)}$
0.1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.2	0.0154	−0.0003	0.0002	0.0004	0.0012	0.0006	0.0017
0.4	0.0316	−0.0002	0.0004	0.0008	0.0018	0.0015	0.0030
0.6	0.0410	0.0002	0.0010	0.0016	0.0032	0.0031	0.0050
0.8	0.0473	0.0007	0.0017	0.0034	0.0050	0.0054	0.0077
1.1	0.0546	0.0022	0.0030	0.0060	0.0078	0.0086	0.0116
2.1	0.0705	0.0074	0.0082	0.0159	0.0182	0.0207	0.0256
3.1	0.0804	0.0132	0.0140	0.0250	0.0285	0.0344	0.0396

$m_o = 0.01$

		KCl		NaCl		LiCl	
m + 0.1	$E_K = E_{Cl}$	E_H	$E_{H(s)}$	E_H	$E_{H(s)}$	E_H	$E_{H(s)}$
0.01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.02	0.0169	−0.0014	−0.0003	−0.0013	−0.0003	−0.0013	−0.0003
0.05	0.0389	−0.0028	−0.0006	−0.0025	−0.0007	−0.0023	0.0005
0.1	0.0552	−0.0036	−0.0014	−0.0032	−0.0006	−0.0030	0.0012
0.2	0.0711	−0.0040	−0.0021	−0.0035	−0.0002	−0.0029	0.0020
0.5	0.0921	−0.0037	−0.0015	−0.0022	0.0014	−0.0010	0.0045
1.	0.1078	−0.0013	0.0016	0.0022	0.0058	0.0048	0.0104
2.	0.1243	0.0044	0.0073	0.0115	0.0154	0.0171	0.0231
3.	0.1349	0.0091	0.0126	0.0211	0.0254	0.0303	0.0368

Part II. Hydroxide System

$m_o = 0.1$

			KCl		NaCl		LiCl	
m + 0.1	E_{Na}	E_{Li}	E_{OH}	$E_{OH(s)}$	E_{OH}	$E_{OH(s)}$	E_{OH}	$E_{OH(s)}$
0.1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.2	0.0164	0.0182	−0.0012	−0.0007	−0.0022	−0.0022	−0.0040	−0.0040
0.4	0.0328	0.0364	−0.0023	−0.0015	−0.0035	−0.0038	−0.0080	−0.0085
0.6	0.0429	0.0480	−0.0027	−0.0018	−0.0045	−0.0050	−0.0105	−0.0116
0.8	0.0500	0.0572	−0.0027	−0.0016	−0.0054	−0.0063	−0.0135	−0.0144
1.1	0.0587	0.0675	−0.0027	−0.0016	−0.0065	−0.0077	−0.0167	−0.0188
2.1	0.0783	0.0948	−0.0012	0.0000	−0.0098	−0.0112	−0.0284	−0.0316
3.1	0.0957	0.1176	0.0017	0.0030	−0.0148	−0.0145	−0.0398	−0.0420

$m_o = 0.01$

			KCl		NaCl		LiCl	
m + 0.1	E_{Na}	E_{Li}	E_{OH}	$E_{OH(s)}$	E_{OH}	$E_{OH(s)}$	E_{OH}	$E_{OH(s)}$
0.01	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.02	0.0169	0.0169	−0.0020	−0.0018	−0.0020	−0.0020	−0.0020	−0.0020
0.05	0.0392	0.0392	−0.0042	−0.0036	−0.0045	−0.0045	−0.0045	−0.0045
0.1	0.0560	0.0561	−0.0054	−0.0050	−0.0065	−0.0065	−0.0079	−0.0071
0.2	0.0725	0.0738	−0.0065	−0.0065	−0.0083	−0.0083	−0.0117	−0.0114
0.5	0.0943	0.0985	−0.0097	−0.0097	−0.0105	−0.0108	−0.0175	−0.0185
1.	0.1119	0.1199	−0.0080	−0.0080	−0.0126	−0.0141	−0.0244	−0.0244
2.	0.1326	0.1487	−0.0065	−0.0065	−0.0162	−0.0180	−0.0376	−0.0376
3.	0.1465	0.1717	−0.0037	−0.0037	−0.0189	−0.0206	−0.0500	−0.0500

$E_{OH(s)}$ in sodium chloride solutions up to 0.3 M above which concentration it is less negative. It is important to note that E_{OH} is more negative than $E_{OH(s)}$ in potassium chloride solutions but less so in sodium and lithium chloride solutions. This interesting behavior will be explained later.

The results in 0.01 M acid are similar to these except that the differences between E_H and $E_{H(s)}$ are about 1.5 millivolts greater in the concentrated solutions. E_{OH} and $E_{OH(s)}$ of the 0.01 M potassium hydroxide—chloride series are identical. The 0.01 M sodium hydroxide—chloride series are similar to the 0.1 M series. On the other hand, E_{OH} and $E_{OH(s)}$ in the case of the 0.01 M lithium hydroxide chloride series are identical. This apparent inconsistency may be due to an error in the results of Harned and Swindells with amalgam cells containing these mixtures, and therefore at present we shall attach no significance to this coincidence.

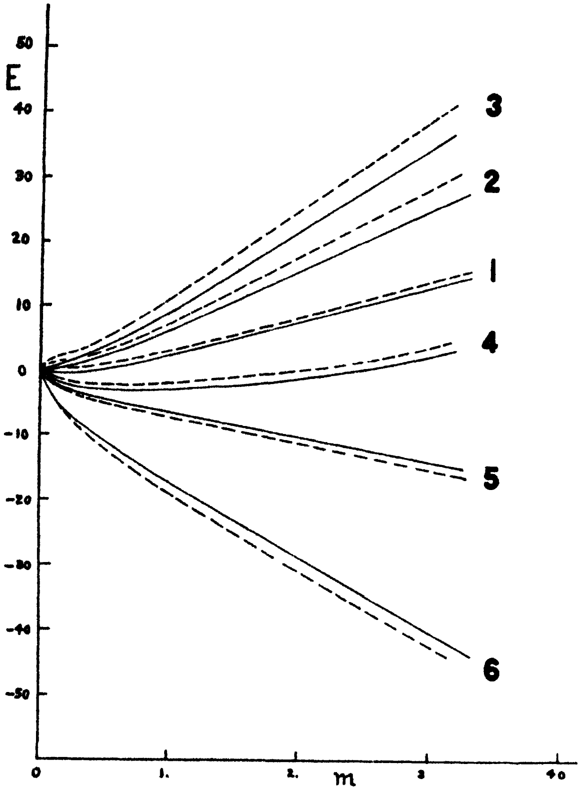


FIG. 1

Electromotive Forces of the Hydrogen and Hydroxyl Ions in Uniunivalent Chloride Solutions.

1. E_H(HCl(0.1), KCl(m))
2. E_H(HCl(0.1), NaCl(m))
3. E_H(HCl(0.1), LiCl(m))
4. E_{OH}(KOH(0.1), KCl(m))
5. E_{OH}(NaOH(0.1), NaCl(m) ,
6. E_{OH}(LiOH(0.1), LiCl(m))

On account of the difficulties inherent in judging the magnitudes of the liquid junction potentials, and the nature of liquid junction potential calculations by means of thermodynamics, it would be wrong to regard this uniformity of behavior as an exact proof but rather as a qualitative indication. It is improbable, on the other hand, that such a distribution of curves is purely fortuitous. In our previous articles on this subject, these postulates have been regarded as an approximation in the more concentrated solutions and as becoming more exact as the salt concentration is decreased.

(3) *Analysis of the Liquid Junction Potentials.*

(a) Some Qualitative Considerations

Let us first consider the electromotive forces of the cells

$$H_2 \mid HCl(0.1) \mid KCl(sat) \mid HCl(0.1),MCl(m) \mid H_2,$$

represented in Fig. 1 by the dotted lines. In the cases of potassium, sodium, and lithium chlorides, the anion has a greater mobility than the cations, although the difference is very small in case of potassium chloride. The addition of the salt will charge the saturated potassium chloride solution negatively to the acid-salt solutions, and small liquid junction potentials would be produced which would cause a positive electromotive force from left to right within the cell. Thus, in all cases, these electromotive forces would be greater than the calculated electromotive forces of the cells

$$H_2 \mid HCl(0.1) \mid HCl(0.1),MCl(m) \mid H_2.$$

From inspection in Fig. 1, we find that the values of the cells containing the saturated chloride are always somewhat more positive than the calculated values, and that the differences between $E_{H(s)}$ and E_H are greater in the order potassium, sodium, lithium chlorides as would be expected since the differences in mobilities of the anion and cation of these salts vary in the same order.

The electromotive forces of the cells

$$H_2 \mid MOH(0.1),MCl(m) \mid KCl(sat) \mid MOH(0.1) \mid H_2$$

are given by the dotted lines 4, 5 and 6 in Fig. 1. In these cases, by similar reasoning, the addition of the salt should increase the negative electromotive force, and the dotted lines should lie below the calculated values. This is found to be true in the concentrated solutions for the sodium hydroxide—sodium chloride, lithium hydroxide—lithium chloride cells, but not for those containing potassium hydroxide—chloride mixtures. This would appear to be an inconsistency in the results but will be seen to disappear when we come to consider the situation more carefully. The negative increase in liquid junction potential is greater for lithium than for sodium than for potassium chloride which would be expected from the mobilities.

Another important point concerning the plots in Fig. 1 should be considered. The dotted and smooth curves diverge from one another up to about 0.5 M and then run nearly parallel to one another in all six cases. Since the liquid junction potential in any case will be a function of the logarithm of the ratios of two concentrations, it is obvious that it will change the least throughout the concentration ranges where the concentration ratio varies the least.

This fact is qualitatively in agreement with the calculations of liquid junction potentials by either Planck's equation[1] or Henderson's equation[2].

Exactly similar considerations hold for the 0.01 M acid-salt series in which case, however, the differences between $E_{H(s)}$ and E_H are somewhat greater. This behavior is also to be expected. $E_{OH(s)}$ is identical with E_{OH} for the 0.01 M potassium hydroxide—chloride series. This indicates a greater negative liquid potential change than in the case of the 0.1 M series. $E_{OH(s)}$ differs from E_{OH} by a slightly greater negative amount in the 0.01 M than in the 0.1 M sodium hydroxide—chloride series. These results, therefore, agree with the ordinary qualitative considerations of the liquid junction behaviors.

(b) Analysis of the Thermodynamic Method of computing Liquid Junction Potentials.

Let us bring together two solutions containing ions of different kinds of which the ion i is of the i^th^ kind. Let us assume that between solution 1 and solution 2 there is a uniform mixing according to the assumption employed by Henderson. Across the boundary, the decrease in free energy accompanying the reversible transfer of 1 Faraday at constant temperature and pressure will be

$$(-\mathrm{dF}) = NFdE_e = -\Sigma\, \mathrm{RTt_i d \ln a_i} \qquad (5)$$

where t_i and a_i are the transference number and activity of the ion of the i^{th} kind. The summation is to be taken for all the ions. The liquid junction potential, E_l, may then be evaluated by integrating each integral throughout the region of mixing or between the limits 1 and 2 where 1 refers to solution 1 and 2 to solution 2. Thus

$$E_l = -\Sigma \frac{\mathrm{RT}}{NF} \int_1^2 \mathrm{t_i d \ln a_i} \qquad (6)$$

or for univalent ions which is the only case we shall consider,

$$E_l = -\Sigma\, 0.05915 \int_1^2 \mathrm{t_i\, d \log a_i} \qquad (7)$$

Now, since log a_i becomes minus infinity as m_i becomes zero, it is more convenient for our purposes to make use of the definition, $a_i = \gamma_i m_i$, and split equation (7) into two parts, one of which contains only the activity coefficients γ_i, and one which contains the molal concentrations, m_i. Thus, we obtain

$$E_l = -\left[\Sigma\, 0.05915 \int_1^2 \mathrm{t_i\, d \log} \gamma_i + \Sigma\, 0.05915 \int_1^2 \mathrm{t_i\, d \log m_i}\right] \qquad (8)$$

The first integral may be more easily obtained than the integral of (7) since γ_i for a single electrolyte is defined so as to equal 1 when m_i equals zero. The second integral of equation (8) is recognized to be that which Henderson evaluated except that we shall employ molal concentrations. Thus, the second part of E_l which we shall denote E_m will be given by Henderson's equation, or

---

[1] Wied. Ann., **39,** 161 (1890); **40,** 561 (1890).

[2] Z. physik. Chem., **59,** 118 (1907); **63,** 325 (1908).

$$E_m = -0.05915 \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \log \frac{U_1' + V_1'}{U_2' + V_2'}$$

where

$$\begin{aligned} U_1' &= U_1 = u_1m_1 + u_2m_2 + u_3m_3 + \cdots \\ V_1' &= V_1 = \bar{u}_1\bar{m}_1 + \bar{u}_2\bar{m}_2 + u_3\bar{m}_3 + \cdots \\ U_2' &= U_2 = u_1'm_1' + u_2'm_2' + \bar{u}_3'm_3' + \cdots \\ V_2' &= V_2 = \bar{u}_1'\bar{m}_1' + \bar{u}_2'\bar{m}_2' + \bar{u}_3'\bar{m}_3' + \cdots \end{aligned}$$

and where U_1, etc. refer to solution 1, U_2 etc. to solution 2, u_1 and $\bar{u}_1$ etc. are the mobilities of the cations and anions in solution 1, and $\bar{u}_1'$ and $\bar{u}_1'$ etc. are the mobilities of the same in solution 2. The second term on the right of (8) may be regarded as solved if our assumption concerning the mixing of the solutions is correct, and we may write

$$E_l = -\left[\Sigma\, 0.05915 \int_1^2 t_i \, d \log \gamma_i + E_m\right] \qquad (9)$$

The summation of the integrals in this equation is the value which we must add to E_m in order to obtain E_l.

Equation (9) contains a part which depends on the concentrations of the ions, but it also contains a part which is a function of the "γ_is" or the thermodynamic coefficients of each of the ions taken individually. Thus in order to obtain E_l, we must know the "γ_is" but in order to evaluate the "γ_is" by this thermodynamic method, we must know E_l. Thus, thermodynamics leads us into a circular situation from which it is at once clear that the above qualitative discussion cannot be regarded as a proof of our postulates. All we can say is that such a uniform distribution of the results for E_H, E_{OH}, and $E_{H(s)}$, $E_{OH(s)}$ would not be obtained if our postulates were not a first approximation. Further, any postulates which lead to the evaluation of the individual ion activities are equivalent to an evaluation of the liquid junction potentials. That is to say, if we should employ values of the activity coefficients of the individual ions calculated by our postulates in equation (9), we should obtain values of E_l which should be just equal to the estimated liquid junctions if our experimental results are consistent and if we are measuring reversible electromotive forces. To illustrate, if from the values of the activity coefficients of the hydrogen, potassium and chloride ions throughout the mixtures HCl(0.1), MCl(m) to KCl(sat) were evaluated by means of our postulates and E_l then calculated by equation (9), then E_l would be found to equal $E_{H(s)} - E_H$. From this, we see that it is illegitimate to use equation (9) in order to verify our postulates.

Then, to what end may we employ this general thermodynamic equation? The answer is merely to test whether the estimated liquid junction potentials agree with the Henderson assumption regarding the mixing of the solutions, to test the consistency of the experimental results, and to show that such apparent anomalies as the distribution of curves of E_{OH} and $E_{OH(s)}$ for the potassium and sodium chloride solutions (Fig. 1) are really not anomalies or caused by experimental error. Further, it is instructive to carry the thermodynamic analysis of liquid junction potentials further than Henderson, and thus show the approximate nature of Henderson's equation. To this end, we shall employ equation (9) in a further analysis of the simplest liquid junctions which we have to consider.

(c) Analysis of the Liquid Junction Potentials at the Boundaries:

$$HCl(0.1), KCl(m) \mid KCl(sat)$$

where *m* is varied from 0 to 3.

Since we are dealing with ratios of ionic mobilities, we have employed the ionic conductances at 18° in place of the mobilities. The ratios of these quantities do not vary greatly between 18° and 25°. Thus, we have taken Λ_H, Λ_K, and Λ_{Cl} to be 314.5, 64.5, and 65.5, respectively, and employed these in calculating the transference numbers[1]. We have also taken the mobilities to be invariant with respect to the total concentration. All concentrations are expressed in mols per 1000 gs. water.

E_m was calculated by Henderson's formula at 0, 0.3, 0.5, 1, 2, and 3M potassium chloride concentrations and the values obtained are given in the second column of Table V.

We have now to determine the value of the integrals, $E_{\gamma_i} = 0.05915 \int_1^2 t_i d \log \gamma_i$ for the hydrogen, potassium, and chloride ions and sum them up according to equation (9). Since the integration is to extend between solution 1 and solution 2, it is necessary to know $\log \gamma_i$ as a function of t_i throughout the intermediate solutions for each of these ions. Since we have no analytical expression for this variation, we have resorted to a graphical integration. That is, we have plotted t_i against $\log \gamma_i$ for the three ions and for values of m equal to 0.0, 0.3, 0.5, 1, 2, and 3, and determined the integrals by evaluating the corresponding areas.

Firstly, it is necessary to evaluate $\log \gamma_i$ at definite total concentrations between solution 1 and solution 2. Thus, if solution 1 is HCl(0.1),KCl(0.3), then in mixing all total concentrations between 0.4 and 4.8, or pure saturated potassium chloride will occur. Now, we make the following assumptions:

(1) γ_H throughout these mixtures of decreasing hydrochloric acid content is the same as in a mixture of 0.1 acid and potassium chloride at the same total concentration. This is known to be very nearly true as a result of the law of the linear variation of $\log \gamma$ at a given total concentration[2]. According to this law, there is little difference between $\log \gamma_H$ in a 0.1 acid − (m) salt mixture and a 0.0 acid − (m + 0.1) salt mixture.

(2) γ_K equals γ_{Cl} at the same total concentration. Thus, γ_K in HCl(0.1), KCl(m) equals γ_{Cl} in this mixture. When m equals zero, γ_K will equal γ_{Cl} in 0.1 HCl. This is our postulate (2).

---

[1] Since the final values for E_l are small, no great error is caused by these assumptions. All calculations were made with a 20-inch slide rule.

[2] Harned: J. Am. Chem. Soc., **48**, 326 (1926).

The values of γ_i and $\log \gamma_i$ obtained by the use of these assumptions are given in Table III.

TABLE III

Activity Coefficients of the Hydrogen, Potassium, and Chloride Ions

m	$E_{H(1)}$	γ_H	$\log \gamma_H$	$\gamma_K = \gamma_{Cl}$	$\log \gamma_K = \log \gamma_{Cl}$
0.0	0.0000	0.842	9.925	0.779	9.891
0.3	−0.0002	0.835	9.922	0.675	9.829
0.5	0.0002	0.849	9.929	0.645	9.810
1.	0.0022	0.920	9.968	0.608	9.784
2.	0.0077	1.136	0.0555	0.566	9.756
3.	0.0128	1.385	0.141	0.577	9.761
4.8	0.0220	1.985	0.298	0.620	9.792

It is now necessary to calculate the "t_is" throughout the mixtures. In the present case

$$t_H = \frac{\Lambda_H m_{H(1)} x}{\Sigma \Lambda_i m_{i(1)} x + \Sigma \Lambda_i m_{i(2)} (1-x)} = \frac{\Lambda_H m_{H(1)} x}{S}$$

$$t_{Cl} = \frac{\Lambda_{Cl} m_{Cl(1)} x + \Lambda_{Cl} m_{Cl(2)} (1-x)}{S}$$

$$t_K = \frac{\Lambda_K m_{K(2)} (1-x)}{S}$$

where x is the degree of mixing or the percentage of solution 1 in the mixed layer divided by 100 at the concentration in question. Thus, if we consider the boundary HCl(0.1) | KCl(4.8), we have all the intermediate mixtures between these concentrations. We select convenient total concentrations such as 0.4, 0.6, etc. and calculate x by assuming a uniform mixing law. Thus, we find that at 0.4 M, x equals 0.937, at 0.6 M, x equals 0.895 etc. These values are sufficient for calculating the "t_is" of our first integral. Then, in a similar manner, we consider the boundary HCl(0.1),KCl(m) | KCl(4.8), compute the degrees of mixing and calculate the "t_is" at 0.6 M, 1.1 M total concentrations etc, etc. All these results are given in Table IV. The first column contains the values of m at the intermediate concentrations. The columns with Roman numerals contain the values of the "t_is" at the total concentrations m. I, II, III, IV, V, and VI refer to the boundaries: HCl(0.1),KCl(m) | KCl(4.8) where the solutions 1 contain salt at concentrations 0.0, 0.3, 0.5, 1, 2, and 3, respectively. Thus, if we consider the boundary HCl(0.1),KCl(0.5) | KCl (4.8), in an intermediate solution at a total concentration of 2, t_H, t_K, t_{Cl} will be 0.073, 0.455, 0.473, respectively. I, II, etc. are the values which we shall employ in our integrals and which we shall designate integrals I, II, etc.

---

[1] This calculation was made before Table II in this paper was compiled. The values of E_H are somewhat different from those in Table II.

TABLE IV

Transference Numbers of the Hydrogen, Potassium, and Chloride Ions

			t_H			
m	I	II	III	IV	V	VI
0.0	0.828	——	——	——	——	——
0.3	0.394	0.408	——	——	——	——
0.5	0.283	0.294	0.305	——	——	——
1.	0.154	0.161	0.170	0.187	——	——
2.	0.051	0.068	0.073	0.080	0.105	——
3.	0.029	0.030	0.032	0.036	0.049	0.073
4.8	0.0	0.0	0.0	0.0	0.0	0.0

			t_K			
m	I	II	III	IV	V	VI
0.0	0.0	——	——	——	——	——
0.3	0.260	0.251	——	——	——	——
0.5	0.327	0.320	0.313	——	——	——
1.	0.404	0.400	0.394	0.384	——	——
2.	0.458	0 457	0.455	0.448	0.433	——
3.	0.479	0.478	0.477	0.475	0.467	0.452
4.8	0.496	0.496	0.496	0.496	0.496	0.496

			t_{Cl}			
m	I	II	III	IV	V	VI
0.0	0.172	——	——	——	——	——
0.3	0.346	0.340	——	——	——	——
0.5	0.391	0.386	0.381	——	——	——
1.	0.442	0.438	0.436	0.429	——	——
2.	0.478	0.475	0.473	0.472	0.462	——
3.	0.499	0.491	0.491	0.489	0.484	0.476
4.8	0.504	0.504	0.504	0.504	0.504	0.504

In Figs. 2 and 3, the values of log γ_i in Table III have been plotted against the values of t_i in Table IV. Integral I refers to the boundary HCl(0.1) | KCl(4.8), integral II to the junction HCl(0.1),KCl(0.3) | KCl(4.8), etc., up to integral VI which corresponds to HCl(0.1),KCl(3) | KCl(4.8). There are in all 18 integrals, six for each ion. The scale was chosen so that 100 sq. cm. equalled 0.000296 volt. Each integral is designated according to the ion considered. Thus H-I is the first integral of the hydrogen ion. 1 and 2 refer to solutions 1 and 2. The sign of the integral is also given. From these plots the values of the integrals were obtained by counting squares, and these in volts are given in Table V. These are added to E_m, and their negative according to equation (9) is E_l.

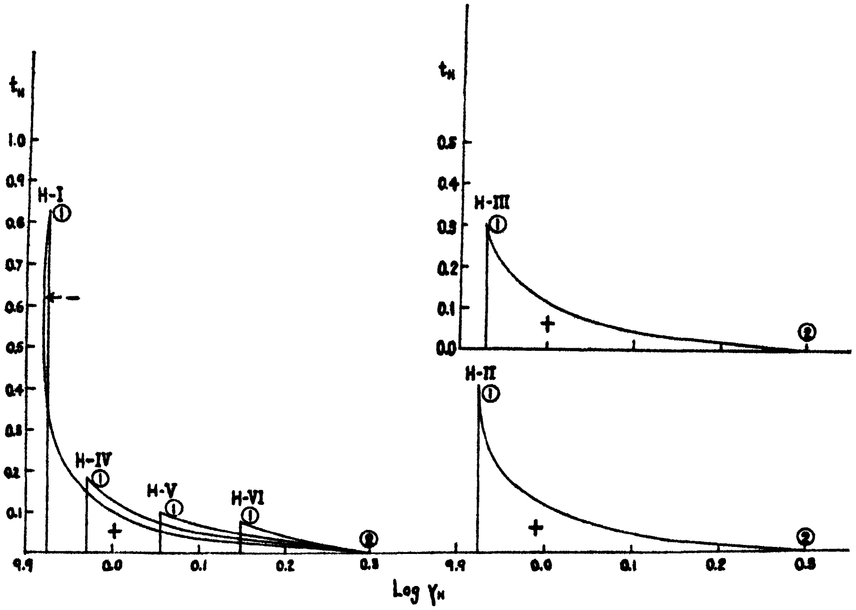


FIG. 2
Hydrogen Ion Integrals

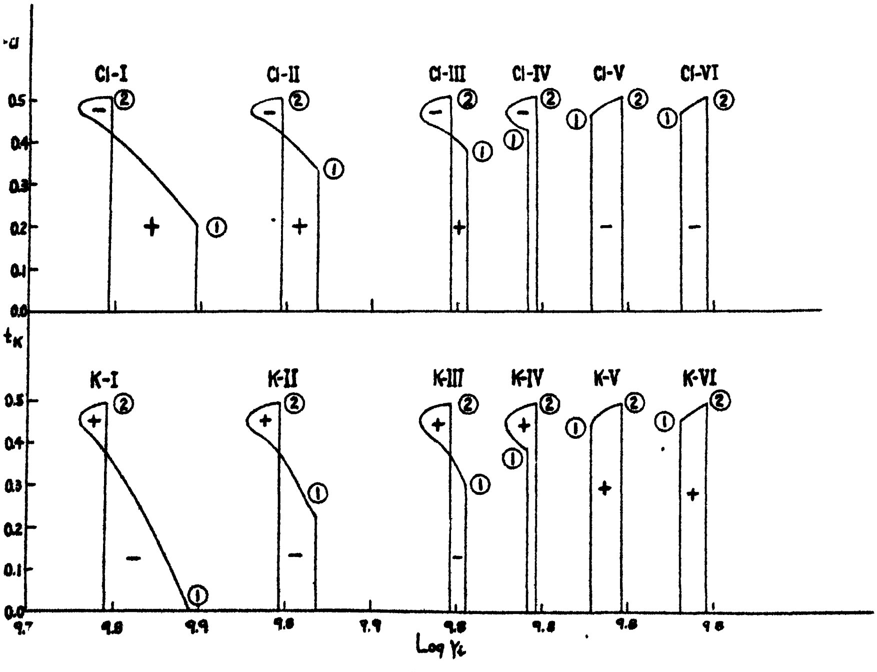


FIG. 3
Potassium and Chloride Ion Integrals

TABLE V

Liquid Junction Potentials by Equation (9)

m	E_m	$E_{\gamma(H)}$	$E_{\gamma(K)}$	$E_{\gamma(Cl)}$	E_l	ΔE_l	$E_{H(s)}$-E
0.0	−0.00363	0.00130	−0.00103	0.00178	0.00158	0.00000	0.0000
0.3	−0.00289	0.00152	−0.00053	0.00085	0.00105	0.00052	0.0006
0.5	−0.00258	0.00148	−0.00021	0.00042	0.00089	0.00069	0.0008
1.	−0.00192	0.00107	−0.00038	−0.00035	0.00082	0.00076	0.0008
2.	−0.00161	0.00060	0.00104	−0.00088	0.00085	0.00073	0.0008
3.	−0.00123	0.00027	0.00087	−0.00083	0.00082	0.00076	0.0008

In the next to last column, the values of ΔE_l or the calculated sum of the liquid junction potentials

$$\mathrm{HCl(0.1)} \mid \mathrm{KCl(sat)} \mid \mathrm{HCl(0.1),KCl(m)}$$

are given. These are positive and agree very well as they should with the differences $E_{E(s)}$-E_H computed from the results in Table II and given in the last column.

It is very important to emphasize at this juncture the fact previously mentioned that this does not constitute a proof of the second of our postulates. To illustrate this, another calculation was made in which we assumed that E_H was 0.0003, 0.0005, 0.001, 0.002, and 0.003 volts less than in our first calculation at 0.3, 0.5, 1, 2, and 3 M salt concentrations. With these new values, log γ_H, log γ_K, and log γ_{Cl} were calculated, and the above calculation of E_l repeated. We obtained 0.0012, 0.0013, 0.0016, 0.0030, and 0.0035 for ΔE_l which agree as well as could be expected with the new values of $E_{H(s)}$-E_H, namely, 0.0009, 0.0013, 0.0018, 0.0028, and 0.0038 volts at values of m equal to 0.3, 0.5, 1, 2, 3, respectively.

(d) Analysis of the Liquid Junction Potentials at the Boundaries:

$$\mathrm{KOH(0.1),KCl(m)} \mid \mathrm{KCl(sat)}$$

In a similar manner, we have computed the liquid junction potentials at the boundaries between potassium hydroxide—chloride solutions and saturated potassium chloride. As in the first calculation we have assumed that log γ_K equals log γ_{Cl} at a given concentration. Λ_{OH} has been taken to be 174. In Fig. 4, the values of log γ_{OH} are shown plotted against t_{OH}. The plots for the potassium and chloride ions are similar to those in Fig. 3 so they have not been given. The integrals I-OH and II-OH differ considerably from the corresponding ones for the hydrogen ion in Fig. 2, and also from each other. Thus, as shown by Table VI, the first of these integrals equals 0.00106 and the second equals −0.00006 volts. This has an effect which causes the sign of ΔE_l to be opposite to that which would be obtained by Henderson's equation, or which would be expected from the ordinary qualitative considerations. The values of E_m, $E_{\gamma(i)}$, E_l, ΔE_l and $E_{OH(s)} - E_{OH}$ are given in Table VI.

TABLE VI

Calculations according to Equation (9)

m	E_m	$E_{\gamma(OH)}$	$E_{\gamma(K)}$	$E_{\gamma(Cl)}$	E_l	ΔE_l	$E_{OH(s)} - E_{OH}$
0.0	0.00088	+0.00106	−0.00218	0.00130	−0.00106	0.00000	0.0000
0.3	0.00066	−0.00006	−0.00085	0.00070	−0.00045	0.00061	0.0007
0.5	0.00063	−0.00021	−0.00040	0.00029	−0.00031	0.00073	0.0009
1.	0.00056	−0.00024	0.00042	−0.00035	−0.00032	0.00079	0.0011
2.	0.00049	−0.00016	0.00104	−0.00119	−0.00033	0.00083	0.0012
3.	0.00046	−0.00006	0.00090	−0.00110	−0.00039	0.00087	0.0013

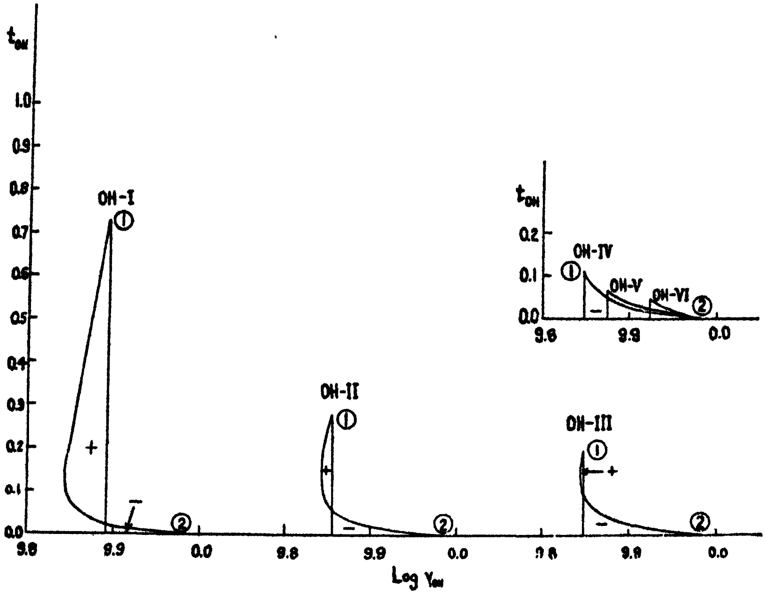


FIG. 4
Hydroxyl Ion Integrals

In order to fit the previous conventions, ΔE_l is obtained by subtracting $E_{l(o)}$ from $E_{l(m)}$, is positive, and corresponds to the sum of the liquid junction potentials of the system

$$KOH(0.1),KCl(m) \mid KCl(sat) \mid KOH(0.1).$$

The agreement between ΔE_l and $E_{OH(s)} - E_{OH}$ is again very good considering the complicated calculation. It is particularly interesting to note that the sign of $E_{OH(s)} - E_{OH}$ which at first glance appeared to be anomalous agrees with the calculated by the general equation.

A like consistency was found for similar calculations of the potentials HCl(0.01), KCl(m) | KCl(sat), and KOH(0.01), KCl(m) | KCl(sat). Cases of the junctions such as HCl(0.1), NaCl(m) | KCl(sat) are much more complicated involving as they do four ions, and a knowledge of the variation of γ_{Na} and γ_K in mixed potassium and sodium chloride solutions. A simple but approximate mixture law was assumed, and a similar calculation was made for the junctions, HCl(0.1), NaCl(m) | KCl(sat), HCl(0.1), LiCl(m) | KCl (sat), etc. Suffice it to say that fairly good agreements between $E_{H(s)} - E_H$ and ΔE_l were obtained.

(e) A Summary of the Above Analysis of the Thermodynamic Calculation of Liquid Junction Potentials.

(1) It is shown that Henderson's equation does not give the liquid junction potential but only part of it. The other part can only be determined thermodynamically by the evaluation of the expression

$$\Sigma\, 0.05915 \int_1^2 t_i d \log \gamma_i.$$

To do this, a knowledge of the individual activity coefficients, the "γ_is", of all the ions involved must be known as a function of the transference numbers, the "t_is", throughout all mixtures between solutions 1 and 2.

(2) Henderson's assumption of uniform mixing of the two solutions leads to correct results as far as can be determined by the above data. In other words, the method of measuring the liquid junctions here employed seems to agree with Henderson's mixing assumption.

(3) The calculations prove that our experimental results are consistent· This is important since it is good evidence that we are measuring reversible electromotive forces in all cases.

(4) The "apparent anomaly" of the sign of the liquid potentials of the junctions, KOH(0.1), KCl(m) | KCl(sat) | KOH(0.1), is shown to be in accord with calculations by the general equation.

(5) It is shown that the thermodynamic liquid junction calculation cannot be used to prove or disprove the validity of postulates I and II. Our earlier conclusions on the question of the independent ion activities depend only on the conviction that unless these postulates are an approximation, the distribution of the curves in Fig. 1 would not be observed. This is a point which we have had in mind from the beginning of these investigations.

(4) *Comparison with the Results of the General Theory of Debye and Hückel:*

In a recent publication, Hückel[1] has considered the problem of the individual ion activity coefficients in the light of his extension of the theory of Debye and Hückel[2], and as a result has found a qualitative but not a quantitative agreement with the postulate of the additivity of the relative partial free energies of the ions of the alkaline chlorides and hydrochloric acid. In view of the difficulty in obtaining the individual activity coefficients by direct measurement which certainly has been made obvious by the preceding discussion of the liquid junction potentials, this qualitative agreement is encouraging. It will therefore be of considerable interest to compare the results obtainable from Debye and Hückel's theory with those derived by means of our postulates. To do this, we shall calculate the chloride ion activity coefficients of the chlorides by Hückel's general equations.

---

[1] Physik. Z., **26**, 93 (1925).

[2] Physik. Z., **24**, 185 (1923).

Following Hückel's procedure, we let

$$\log f_{Cl} = \log f^{\circ}_{Cl} + \log f^{x}_{Cl} \qquad (10)$$

where f_{Cl} is equal to a^1_{Cl}/N where a^1_{Cl} is the activity of the chloride ion and N is mol fraction. From f_{Cl}, γ_{Cl} or a^1_{Cl}/m may be obtained by the equation

$$\log \gamma_{Cl} = \log f_{Cl} - \tfrac{1}{2} \log (1 + 0.036m). \qquad (11)^1$$

From equations (64), (68), and (85a) in Hückel's paper, we obtain

$$\begin{aligned} \log f^{o}_{Cl} = {} & - 0.354 \sqrt{\Gamma}\; 2 \left[\frac{1}{2\, x^{o}_{Cl}} - \frac{1}{x^{o2}_{Cl}} + \frac{1}{x^{o3}_{Cl}} \operatorname{lu} (1 + x^{o}_{Cl})\right] \\ & + \frac{3}{2}\left[\frac{1}{x^{o2}_{Cl}} + \frac{1}{x^{o2}_{Cl}}\,\frac{1}{1+x^{o}_{Cl}} - \frac{2}{x^{o3}_{Cl}} \operatorname{lu} (1 + x^{o}_{Cl})\right] \\ & + \frac{3}{2}\left[\frac{1}{x^{o2}_{M}} + \frac{1}{x^{o2}_{M}}\,\frac{1}{1+x^{o}_{M}} - \frac{2}{x^{o3}_{M}} \operatorname{lu} (1 + x^{o}_{M})\right] \qquad (12)^{*} \end{aligned}$$

where Γ equals 2c, and

$$x^{\circ} = 0.232 \times 10^{8}\, a_i \sqrt{2c}$$

where a_i is the apparent ionic diameter of the ion and c is the normal concentration.

According to equation (85b) in Hückel's paper, we obtain

$$\begin{aligned} \log f^{x}_{Cl} = {} & 0.0194 \times 10^{-8}\, \Gamma \Bigg[\frac{1}{a_{Cl}}\, \frac{1}{1 + A_{Cl}\sqrt{2c}}\, \frac{\delta_M + \delta_{Cl}}{2} + \frac{\delta_{Cl}}{2} \bigg[\frac{1}{a_{Cl}} \\ & \frac{1}{1 + A\sqrt{2c}} + \frac{1}{a_M}\, \frac{1}{1 + A_M\sqrt{2c}} \bigg] \Bigg] - 0.00225\, \Gamma^{3/2}\, \frac{\delta_M + \delta_{Cl}}{2} \bigg[\frac{1}{2} \\ & \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} + \frac{1}{2}\, \frac{1}{[1 + A_M\sqrt{2c}]^2} \bigg] + 0.000246 \times 10^{-8}\, c^2 (\delta_M + \delta_{Cl}) \\ & \Bigg\{ \frac{1}{a_{Cl}} \bigg[3/4\, \frac{1}{1 + A_{Cl}\sqrt{2c}} + \frac{1}{4}\, \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} \bigg] (\delta_M + \delta_{Cl}) + \frac{2\delta_{Cl}}{a_{Cl}} \bigg[3/4 \\ & \frac{1}{1 + A_{Cl}\sqrt{2c}} + 1/4\, \frac{1}{[1 + A_{Cl}\sqrt{2c}]^2} \bigg] + \frac{2\delta_{Cl}}{a_M} \bigg[3/4\, \frac{1}{1 + A_M\sqrt{2c}} + \frac{1}{4} \\ & \frac{1}{[1 + A_M\sqrt{2c}]^2} \bigg] \Bigg\} \qquad (13) \end{aligned}$$

---

[1] Scatchard: J. Am. Chem. Soc., 47, 2098 (1925); Harned: 48, 326 (1926).

* The second member on the right of Equation (68) in Hückel's paper should be positive.

In this equation, A_i equals $0.232 \times 10^8 a_i$, and δ_i is a constant characteristic of the effect of the ion on the dielectric constant of the medium.

In this calculation, we have employed the values of the constants obtained in another paper[1]. We have assumed that both the apparent ionic diameters of the potassium and chloride ions and their δ values are identical according to the second of our postulates, and have calculated the values of a_i and δ_i for the other ions upon this assumption. The values of these constants are given in Table VII. By using these constants in equation (11), (12), and (13), the values of γ_{Cl} given in this table were calculated.

TABLE VII

Activity Coefficients of the Chloride Ion in Uniunivalent Chlorides according to Hückel's General Equations

(1) Constants

Ion	$a_i \times 10^8$	δ_i
H^+	3.38	20.6
Li^+	3.84	19.8
Na^+	3.82	8.6
K^+	3.38	3.2
Cl^-	3.38	3.2

(2) γ_{Cl}

c	γ_{Cl} (KCl)	γ_{Cl} (NaCl)	γ_{Cl} (LiCl)	γ_{Cl} (HCl)
0.5	0.654	0.665	0.695	0.700
1.0	0.607	0.629	0.686	0.698
2.0	0.578	0.613	0.747	0.775

As a result, we find that the activity coefficient of the chloride ion is greater in the solution of the electrolyte which has the greater activity coefficient. The differences between the results from Debye and Hückel's theory and our postulate (1) correspond to 0.4, 1.5, 1.8, millivolts at 0.5 N; 0.9, 3.1, and 3.7 millivolts at 1 N; and 1.5, 6.5, and 7.5 millivolts at 2 N in the cases of sodium and lithium chlorides and hydrochloric acid solutions, respectively. To make this comparison more clear, the values of E_H and E_{OH} in the 0.1 M hydrochloric acid-salt mixtures and the 0.1 M hydroxide salt series have been calculated from these values of γ_{Cl} and the results are shown plotted against the molal salt concentrations in Fig. 5. The dashed lines are the values obtained by our postulates and previously shown in Fig. 1. The full lines are those obtained by Hückel's equations.

A small difference in distribution of the curves of E_H and E_{OH} in the potassium and sodium chloride solutions as predicted by the two theories is noticeable. E_H in the lithium chloride solution as predicted by Hückel's equation lies considerably closer to E_H in the sodium chloride solutions than does the dashed line of our earlier theory. The general similarity of distribution of these plots requires no further comment. Like calculations leading to a somewhat closer agreement were obtained for the activity coefficient of the chloride ion in the alkaline earth chloride solutions but this question need not be considered here.

---

[1] J. Am. Chem. Soc., **48**, 0000 (1926).

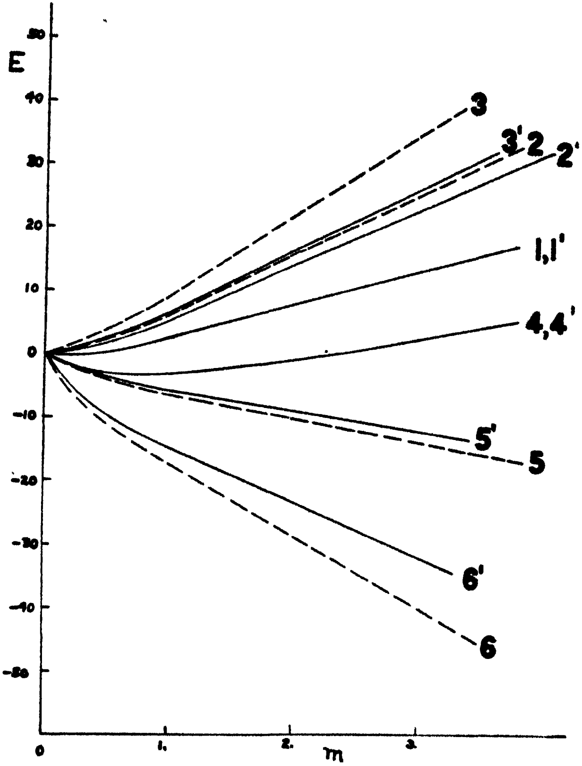


Fig. 5

Comparison of $E_{\rm H}$ and $E_{\rm OH}$ (Fig. 1) with the Values obtained by Hückel's General Equations.

1, 2, 3, 4, 5, and 6, are taken from Fig. 1.

1′, 2′, 3′, 4′, 5′, and 6′, are the curves obtained by Debye and Hückel's general theory.

$1,1^1$ $E_{\rm H}$(HCl(0.1), KCl(m))
$2,2^1$ $E_{\rm H}$(HCl(0.1), NaCl(m))
$3,3^1$ $E_{\rm H}$(HCl(0.1), LiCl(m))
$4,4^1$ $E_{\rm OH}$(KOH(0.1), KCl(m))
$5,5^1$ $E_{\rm OH}$(NaOH(0.1), NaCl(m))
$6,6^1$ $E_{\rm OH}$(LiOH(0.1), LiCl(m))

(5) *Theoretical Considerations:*

In the last section, two series of results were compared, one of which depends on a probable conclusion based on experimental behaviors, and the other derived from a theory. It is not to be expected that the results from either of these methods are exact.

According to Debye and Hückel's theory, the difference between the activity coefficients of univalent ions of different kinds is due, firstly, to the difference in apparent ionic diameters, and, secondly, to the difference in effects of the ions of different kinds on the dielectric constant of the medium. The first of these causes turns out to be small since we find a small difference in ionic diameters of the ions here considered, and therefore this factor will be omitted in the following discussion. Hückel assumes that the dielectric constant, D, of the medium varies according to the linear law

$$D = D_o - \Sigma \delta_i c_i \qquad (14)$$

where D_o is the dielectric constant of the pure solvent, δ_i is a constant characteristic of an ion of the i^{th} kind, and c_i is its concentration. The introduction of this equation into the theory leads to an equation for the activity coefficient of a strong electrolyte containing an approximately linear term which is found to conform with the behavior of uniunivalent and biunivalent chlorides, and hydrochloric acid in chloride solutions. D is supposed to be uniform between all the ions. That is to say the medium is considered macroscopically. δ_i is greater for the ion which appears to cause the greatest electrostriction in its immediate neighborhood. Thus, δ_{Li}: δ_{Na}: δ_K as 19.8: 8.6: 3.2 which is the order of their hydration values[1], a possible measure of electrostriction. This fact would suggest that the change in dielectric constant of the medium is not uniform but is greater in the immediate environment of the ions, or in the regions where the greatest electrostriction would occur, and that when we consider the individual activities, it may be necessary to take a microscopic point of view. According to this theory the variation of these microscopic dielectric constants would be expressed by

$$D_1 = D_o - \delta_1'c \; ; D_2 = D_o - \delta_2'c,$$

and these should be employed separately in calculating the individual ion activities of a uniunivalent electrolyte. Such a theory would lead to a result in conformity with our postulates. But this theory is seen to be an extreme point of view since it requires a change in dielectric constant of the solvent in the immediate neighborhood of the ions while the intermediate solvent is not influenced. Further, in mixtures at the same total concentrations, or total chloride ion concentration, this theory would require that as the cation concentrations were varied, the values of the dielectric constants in the immediate neighborhood of the cations should vary with changing cationic concentrations while that in the neighborhood of the chloride ion would not be influenced. Such a condition would not be expected to be strictly valid.

There is another important consideration which indicates that the true values lie between those calculated by the postulate of additivity and those predicted by Hückel's theory. Equation (14) cannot be valid in very concentrated solutions of electrolytes such as hydrogen, lithium, or calcium chlorides because the calculated δ – values are so high for these electrolytes that the dielectric constant, D, would pass through O and become negative in the neighborhood of 4M lithium chloride and 2M calcium chloride, a condition which is obviously an impossibility. If the general idea of the theory of Debye and Hückel is correct, that is to say that the dielectric constant change is the important factor in the concentrated solutions, then δ_i of the ions such as lithium, hydrogen and calcium ions and also the chloride ions must decrease with increasing concentration. Such a decrease would bring the results of Hückel's into closer agreement with those predicted by the postulate of additivity.

---

[1] Washburn: J. Am. Chem. Soc., 31, 322 (1909); 35, 751 (1913); 37, 694 (1915).

Looked at in this way, it would seem that both "the hypothesis of the independent ion activities" and Hückel's theory are extreme points of view. The first would require only a change in dielectric constant with changing electrolyte concentration in the immediate environment of the ion, the intermediate solvent not being influenced, and the second assumes a uniform dielectric between the ions. Such considerations would lead us to expect that the values of the individual ion activity coefficients should be somewhere between those predicted by these two theories. We have considered this question from the narrow point of view that the dielectric constant is the only factor to be considered. A similar argument could have been made if we had considered another factor or group of factors which would account numerically for the behaviors of these concentrated solutions.

Neither of these theories should be applied to solutions of ions other than the alkaline, alkaline earth metal, hydrogen and halide ions, which are characterized both by their simplicity and the symmetrical space distribution of electron orbits. The more complex ions such as NO_3^-, SO_4^{--} or the unsymmetrical ions such as OH^- do not conform to the principle of additivity or to Debye and Hückel's theory unless some further factor be introduced.

Summary

(1) Measurements of cells of the types

$$H_2 \mid HCl(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$
$$H_2 \mid MOH(m_o),MCl(m) \mid KCl(sat) \mid Hg_2Cl_2 \mid Hg$$

have been revised, completed, and tabulated.

(2) These data have been considered from the point of view of "the hypothesis of the independent ion activity coefficients".

(3) A comprehensive study of the general thermodynamic method of computing liquid junction potentials has been made.

(4) The results from the "hypothesis of the independent ion activities" are compared with those obtained from Hückel's extension of the Debye and Hückel theory.

Philadelphia, Pa.

THE NATURE OF THE STRUCTURE OF CELLULOSE AND ITS SIGNIFICANCE IN CHEMICAL TRANSFORMATIONS*

BY R. O. HERZOG

In the first part of the present paper the previous X-ray spectrographic investigations[1], carried out with untreated and mercerised cellulose respectively, have been controlled, and new evidence obtained as to the behavior of cellulose in the magnetic and electric field.

Further, the results of X-ray analysis of certain derivatives of cellulose (cellulose nitrate and cellulose acetate) are described.

In the second part, a parallel is drawn between the dimensions of crystallites of cellulose and of its derivatives, and the particles found in colloidal solution, and evidence of a relation between the size of particles and the size of molecules is brought forward.

PART I

X-Ray Spectrographic Investigation of Cellulose
(Carried out with W. Jancke)

It has been clearly shown, that cellulose, in its natural condition, consists of aggregates of crystallites as found in the bast fibres, seed hairs, and other plant[2] tissue as well as in the animal body (Tunicin)[3]. In the bast fibres, the crystallites are often arranged with one crystal-axis in the fibre-axis, or, (at any rate those of the same layer) at a definite angle to it; in cotton, they are—with respect to this axis—twisted spiral-like, etc; it may be said with some degree of certainty that the observations made by means of double refraction, and interpreted on the basis of Nägeli's micellar hypothesis,[4] or by the theory of Wiener[5] are completely confirmed by X-ray spectrography.

It is also possible to use the experimental data obtained in the present investigation for a revision of the determination of the crystalline system of cellulose. Since among the bast fibres, ramie, hemp, Titaric[6], broom, and mulberry-tree show the best defined interferences, and the ratio of the distances of these on the equator are identical within the limits of experimental error, these fibres, in addition to that of cotton, were chosen as suitable objects for investigation. In Table I A_1 A_2 . . . indicate the interference points on the equator of the sphere, I, II, III, IV, etc., those on the corresponding hyperbola (layer-lines). Figure 1 shows the crystallographic indices of the points according to Polanyi[4].

---

* Contribution from the Kaiser Wilhelm-Institut für Faserstoffchemie, Berlin-Dahlem.

[1] Z. angew. Chem. **34**, 385 (1921).

[2] Ber. **53**, 2162 (1920); Naturw. **12**, 955 (1924).

[3] Z. physiol. Chem. **141**, 63 (1924).

[4] Sitzungsber. Akad. Wiss. München, **9**, 389 (1879).

[5] Pogg. Ann., **118**, 79 (1863).

[6] A tropical bast fibre placed at our disposal, the exact nature of which it was impossible to ascertain.

The second column records the intensity of the interference spots v.str. = very strong; st. = strong; m. = moderate; w. = weak; v.w. = very weak). D/2 denotes the observed angle of reflection. (Glanzwinkel).

TABLE I

Observed point-positions for natural cellulose using vertical incidence. (Average value)

Point	Intensity	$\sin^2 \theta/2$	Possible error of $\sin^2 \theta/2 \pm$ u. 10^{-4}
A_1	str.	0,01675	3
A_2	m.	0,02105	3
A_3	w.	0,03210	3
A_4	v.str.	0,03923	3
A_5	m.	0,1600	9
I_1	w.	0,01296	10
I_2	m.	0,08940	17
I_3	w.	0,1142	30
II_1	str.	0,03260	6
II_2	s.	0,06480	7
II_3	s.	0,07070	8
II_4	v.w.	0,1335	40
II_5	v.w.	0,1683	80
III_1	m.	0,0604	20
III_2	m.	0,0690	8
III_3	str.	0,0894	10
III_4	w.	0,1332	30
III_5	w.	0,1455	60
IV_1	w.	0,1102	18
IV_2	str.	0,1295	7
IV_3	w.	0,1710	20

Calculations made from these values together with certain other considerations[1], which are reported elsewhere, point to rhombic symmetry. We obtain from these values the quadratic equation

$$4 \sin^2 \theta/2 = 0{,}03210\, h^2 + 0{,}03923\, k^2 + 0{,}02275\, l^2$$

---

[1] Naturw., **12**, 956 (1924).

[2] With monoclinic symmetry, a considerable splitting off of points is to be expected but does not occur. Also it is not possible to include the points A_1 up to A_4, within the limits of experimental error.

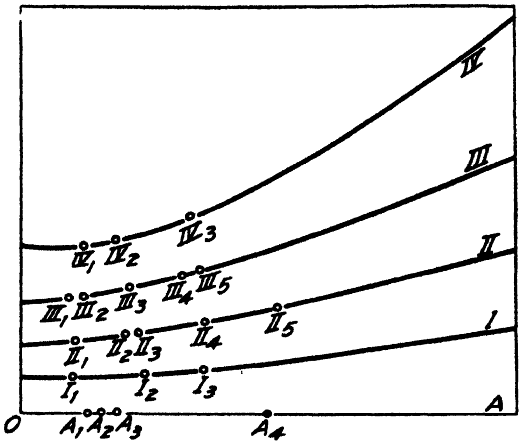


FIG. 1

Diagram of the Cellulose Interference Points in One Quadrant.
O = Point of penetration of the X-ray beam
A = Equator
I, II, III, IV = Layer-lines (hyperbola)
A_1, A_2, A_3, etc. = Positions of interferences.

TABLE II

Rhombic form for 4 molecules

Point	$\sin^2 \theta/2$		Indices
	observed	calculated	
A_1	0,01675	0,01783	110?
A_2	0,02105	—	—
A_3	0,03210	0,03210	200
A_4	0,03923	0,03923	020
A_5	0,1600	0,1569 0,1605	040? 330
I_1	0,01296	0,01371	101
I_2	0,08940	0,08772	311
I_3	0,11420	0,11714	321
II_1	0,03260	0,03255	012
II_2	0,06480	0,06466	212
II_3	0,0707	0,0700	122
II_4	0,1335	0,1342	322
II_5	0,1683	0,1610	412
III_1	0,06040	0,05921	103
III_2	0,06900	0,06902	113
III_3	0,08940	0,09040	023
III_4	0,1332	0,1332	313
III_5	0,1455	0,1395	133
IV_1	0,1102	0,1088	114
IV_2	0,1295	0,1302	024
IV_3	0,1710	0,1730	314

A_1, however, does not fall within the limits of experimental error, and the same is true of A_2; (110) lies between the 2 points, and closer to A_1. It is probable that these discrepancies are due to impurities in the cellulose. Moreover, it appears that the deviations between the calculated and observed values of $\sin^2 \theta/2$ are within the limits of experimental error (strong deviations only at weak intensities).

From the above quadratic equation the following values for the lengths of the edges of the crystallographic unit-cell may be calculated, and these agree fairly well with the numbers previously reported.

$$a = 8{,}60 \,.\, 10^{-8}\ \text{cm},$$
$$b = 7{,}78 \,.\, 10^{-8}\ \text{cm},$$
$$c = 10{,}22 \,.\, 10^{-8}\ \text{cm}.$$

Hence the volume V is 684 . 10^{-24} cm^3, and from the equation

$$\frac{M.n}{N.s} = V,$$

(where M is the molecular weight, $(C_6H_{10}O_5) = 162$; N, Avogadro's number, $= 6{,}06 \,.\, 10^{23}$; s the density of cellulose $= 1{,}52$; and n the number of $(C_6H_{10}O_5)$ — groups united in the cell) it follows, that $n = 3{,}9$; in other words, there are 4 $(C_6H_{10}O_5)$ groups in the unit-cell, as already calculated by Polanyi from our previous measurements. (Error ± 2, 7%)[1].

It has been previously mentioned (l.c.), that with so-called "oblique" photographs, i.e. where the preparation is inclined relative to the X-ray beam, 2 interferences occur, at variance with the calculated value. But a number of other anomalies (splitting off, etc.) are also found. These may be accounted for by assuming the presence of more than one substance—as for example two modifications, which are chemically quite similar. A further explanation is possibly to be found in certain physical phenomena such as the tension produced in the crystallites during their growth. Various factors seem to indicate that both assumptions are probably correct.

X-Ray Analysis of Mercerised Cellulose

When cellulose fibres are mercerised by treating with a strong solution of caustic soda, they give, after removal of the sodium hydroxide with water, a

---

[1] If a greater unit cell, for example one with 16 $(C_6H_{10}O_5)$ groups is assumed to exist, the calculated results are in no better agreement than those tabulated above. But in this case only 27% of the possible interferences are observed, as compared with 72% for 4 $(C_6H_{10}O_5$ radicals). From the evaluation of Debye-Scherrer-diagrams, O. L. Sponsler assumes cellulose to have a tetragonal form. However sufficient reliability as to the position of the interference spots cannot be secured on this basis. Sponsler in fact has only taken into consideration the strongest interferences; the weak ones do not fit in with the quadratic equation.

A quadratic equation for hexagonal symmetry can with good approximation be given, assigning 32 $(C_6H_{10}O_5)$ to the unit cell:

$$4 \sin^2 \theta/2 = 0{,}005135\,(H^2 + k^2 - hk) + 0{,}02275\, l^2.$$

in which case only 25% of the possible positions of points are found.

point-diagram somewhat different from that of the original cellulose, and this difference becomes more pronounced the more complete the mercerisation. This holds especially for fibres which are prevented from shrinking by carrying out the mercerising under tension. With fibres mercerised without tension, distortion of the particles soon occurs, and the interference points degenerate into indistinct arcs. It is possible to follow the progress of the mercerisation by X-ray spectrography.

On the equator, the points A_3 and A_4 exhibit a very different ratio of intensities. This ratio of about 1:5 for untreated cellulose, is changed to 1:2 during the initial stage of mercerisation (i.e. when about 8% sodium hydroxide solution is employed); the positions of these and other interferences of the fibre diagram remain the same. It can even be stated that with only slight mercerisation all points stand out more distinctly, an advantage which is lost and reversed by stronger mercerisation. With the latter, using a concentration of sodium hydroxide of 14% (or a little above) at room temperature, the ratio of the intensities of the points A_3 and A_4 is further altered, but in this case the positions of their interferences also change, the points moving closer to the point of penetration of the primary beam. With total mercerisation, (by means of 28% or even stronger sodium hydroxide solution), the ratio of the above named points, which are now to be named B_3 and B_4, is found to be 1 : 1, these being still closer to the point of penetration.

The equatorial points A_1 and A_2, which as we have already stated, do not fit in with the quadratic equation, are weakened in intensity by progressive mercerisation and finally disappear completely. They also seem to change their positions, in the sense that they move simultaneously somewhat apart.

Only in the final stage of total mercerisation does a new point, B_0, appear on the equator, and this is closer to the point of penetration than any of the other interferences observed, but it does not fit in with any quadratic equation appropriate to mercerised cellulose.

The points on the hyperbola are much weakened in intensity by strong mercerisation, and they move in a manner such that the origin of the hyperbola on which they lie, moves away from the point of penetration.

Table III throws some light on the alteration of the intensities and the displacement of the positions of the most important points. In this table, the various stages of mercerisation are indicated as follows: 0 = untreated; 1 = treated with weak sodium hydroxide solution (8 – 10%); 2 = treated at a concentration of about 14%; 3 = totally mercerised (use of a sodium hydroxide solution of 28% or above).

As all weaker points of the original cellulose diagram gradually disappear with progressive treatment, and only the most intense remain measurable, we have only these few available for the purpose of deriving the quadratic equation for mercerised cellulose.

TABLE III

List of the most essential Point-Positions, and their intensities, with progressive mercerisation.

Point	Stage of treatment	$\theta/2$	Intensity	$\sin^2 \theta/2$ observed	Error	$\sin^2 \theta/2$ calculated (totally mercerised.)
—	0	—	—	—	—	—
—	1	—	—	—	—	—
—	2	—	—	—	—	—
B_0	3	6° 8,5′	w.	0,01143	0,0004	?
A_1	0	7° 26′	str.	0,01675	0,0003	
”	1	”	m.	”	”	
”	2	7° 19′	w.	0,01623	”	
—	3	—	—	—	—	
A_2	0	8° 20′	m.	0,02103	0,0003	
”	1	”	m.	”	”	
”	2	8° 28′	w.	0,02170	”	
—	3	—	—	—	—	
A_3	0	10° 19′	w.	0,03210	0,0003	
”	1	”	m.	”	”	
”	2	10° 14′	str.	0,03160	0,0004	
” = B_3	3	10° 6,5′	str.	0,03080	”	0,03080
A_4	0	11° 25,5′	v.str.	0,03923	0,0003	
”	1	”	str.	”	”	
”	2	11° 12′	str.	0,03760	0,0004	
” = B_4	3	11° 2′	str.	0,03660	”	0.03660
II_1	0	10° 24′	str.	0,03260	0,0006	
”	1	”	str.	”	”	
”	2	10° 31′	m.	0,03330	”	
”	3	10° 33′	w.	0,03350	”	0,03345
III_3	0	17° 24′	str.	0,08940	0,0010	
”	1	”	m.	”	”	
”	2	17° 32′	w.	0,09080	”	
”	3	17° 35′	v.w.	0,09120	”	0,09127
IV_d	0	17° 34′	v.str.	0,09100	0,0008	
”	1	”	v.str.	”	”	
”	2	18° 1′	m.	0,09580	0,0020	
”	3	18° 4′	w.	0,09620	”	0,09720

Assuming a unit-cell with four molecules, and rhombic symmetry, the quadratic equation is given by:

$$4 \sin^2 \theta/2 = 0{,}03080\, h^2 + 0{,}03660\, k^2 + 0{,}02430\, l^2$$

From this quadratic equation a: b: c = 8,88: 8,05: 9,88 is obtained, and the volume V of the unit-cell is seen to be 706 sq. Å.U., a value in exact agreement with that computed from the molecular weight (704).

As already stated, the new point B_0 does not fit in with this form, and is therefore due to the presence of another substance. Possibly it is also related to the points A_1 and A_2 which have disappeared, and which likewise could not be classified. The alteration of the intensities of the points B_3 and B_4, as compared with those of A_3 and A_4, (unless attributed to distension), forces one to the conclusion that the lattice planes are now otherwise occupied.

For the sake of comparison, we have also examined a sample of β-cellulose, prepared from wood cellulose by dissolving in NaOH and reprecipitating, this procedure being repeated three times. The values obtained with mercerised cellulose and with this β-cellulose are shown in the following Table IV (w = weak; str. = strong).

TABLE IV

Mercerised cellulose	β-cellulose
6° 8′ w.	6° 3′ w.
10° 6′ str.	10° 1′ str.
11° 2′ str.	10° 56′ w.
14° 19′ w.	14° 14′ w.
17° 50′ w.	17° 30′ w.
20° 20′ w.	20° 25′ w.

By comparing the dimensions of the unit-cells of the untreated and mercerised cellulose, it appears that the distance along the direction of the fibre has diminished from 10,22 to 9,88 Å.U. This means a contraction of 3% along the direction of the fibre. An even higher value has actually been observed during mercerisation. The horizontal dimensions, however, increase from 8,60 to 8,88 and from 7,78 to 8,05 Å.U.

That the points of mercerised cellulose, as well as the interferences of untreated cellulose do in fact fit in with a rhombic form of the same kind, enhances the probability of the accuracy of this form.

If the dimensions of the crystallites of the untreated cellulose are calculated according to Scherrer's[1] equation from the breadth of suitable interference spots, measured between points at which the intensity has decreased to half of its maximum value, two values, viz., 117 and 66 Å.U. are obtained as maxima. Since marked differences in the intensity of the interference spots do not exist, we may conclude that the third value is substantially the same.

---

[1] Zsigmondy: "Kolloidchemie", Appendix (1920).

Behavior of Natural and Artificial Cellulose Fibres in the Magnetic[1] *and Electric Field.*

Bast fibres proved to be diamagnetic, but bundles of fibres arranged parallel behave like irregular crystals.

In the present investigation parallel-arranged fibres were formed by attaching them to thin plates by means of a solution of gum arabic and then, after hardening, making them plane parallel by strong pressure.

From these plates, thin circular disks 8 mm in diameter were punched by means of a very accurately worked punch, the centres of the disks being simultaneously pierced by a needle, inserted centrally into the punch, so that the plates could be easily attached to the lower end of a straight glass filament about 10 cm in length and 0,5 mm in thickness. To the upper end of the glass-filament, which was suspended on a thin cocoon filament, 30 cm in length, small mirrors of silver-plated cover-glass (about 1 × 4 mm) were cemented, by means of which the deflections and vibrations in all positions of adjustment could be optically observed. The suspension itself was found to be quite satisfactory. The disks under investigation had a mean weight of about 20 mg. They may be regarded as monaxial crystal-plates. They are also to be considered as rather homogeneous, since the embedding medium, gum arabic, was found to have, in the solid state, a refractive index $n_D = 1.51$ as compared with a mean value $n_D = 1.55$ for bast and artificial fibres.

In the magnetic, as well as in the uniform electric field, the orientation of the fibres was parallel to the lines of force.

The difference of the magnetic susceptibilities $(x - x')$ was computed according to Graetz[2]; t_o and t are the times of vibration without and within the field, respectively. The field of force was $3{,}25.10^3$ Gauss.

The electric measurements were carried out in an homogeneous alternating field of 220 v and 50 cycles, with the pole-plates at a distance of 1,2 cm. E_2 and E_1 are the dielectric constants, parallel and perpendicular to the optical axis, respectively.

Table V gives a survey of our experimental results, the optical measurements being also listed. n_{D_1} and n_{D_2} denote the refractive indices with the fibre orientated parallel and perpendicular to the plane of polarisation, respectively.

Table V illustrates the parallelism between the various values characteristic of anisotropy and are in remarkable agreement with the results of our X-ray investigations[3].

The turning moment in the electrical field is so strong that this method may possibly prove of practical value for technical purposes, such as, for example, a method of control in artificial silk manufacture.

---

[1] See J. Pauksch: Akad. Wiss. Wien, Math.-Naturwiss. Kl., **115**, I, 553 (1906).

[2] "Handbuch der Elektrizität und des Magnetismus", **4**, 829.

[3] Kolloid-Z., **35**, 201 (1924).

TABLE V

Magnetic measurements

	$\left(\frac{1}{t^2} - \frac{1}{t_0^2}\right)$	mean error ±	$(x-x').10^6$	mean error %
ramie	0,581	0,0110	0,066	1,9
cuprammonium silk	0,224	0,0115	0,025	5,1
viscose I	0,213	0,0093	0,024	4.4
viscose II	0,090	0,0069	0,010	7,7
viscose film (32% stretched)	0,062	0,0077	0,007	12,5
viscose film (20% stretched)	0,039	0,0083	0,004	21

Dielectric measurements

	$\left(\frac{1}{t^2} - \frac{1}{t_0^2}\right)$	mean error ±	$E_2 - E_1$	mean error %
ramie	0,120	0,004	4,84	10
cuprammonium silk	0,063	0,003	2,54	10
viscose I	0,062	0,002	2,50	4,7
viscose II	0,047	0,002	1.90	2,9
viscose film (32% stretched)	0,027	0,003	1,17	4,9
viscose film (20% stretched)	0,019	0,002	0,77	3,0

Optical measurements[1]

	n_{D_2}	n_{D_1}	Double refraction
ramie	1,5879	1,5331	0,0548
cuprammonium silk	1,5595	1,5249	0,0346
viscose I	1,5560	1,5221	0,0339
viscose II	1,5442	1,5273	0,0169
viscose film (32% stretched)	—	—	0,0115
viscose film (20% stretched)	—	—	0,0064

---

[1] The specific double refraction of the stretched films was determined by means of the Babinet compensator, that of the artificial silk by Becke's method.

Röntgenspectrographic Investigation of Cellulose Nitrate and Cellulose Acetate. *(Carried out with Th. Nickl.)*

According to Hermann Ambronn[1] stretched cellulose nitrate films are doubly refractive, while X-ray investigations indicate an amorphous structure. In agreement with Hans Ambronn[2] it was only found possible to detect a crystalline structure in the case of a nitrocellulose prepared under conditions in which the fibrous structure was maintained and which had not been subjected to any process of solution. The same result was also found with cellulose acetate.[3]

The X-ray investigation of nitrated and of acetylated hemp fibre points to the conclusion, that these two derivatives of cellulose most probably crystallize in the rhombic system.

The dimensions of the unit-cells are approximately as follows:

	(a) cellulose nitrate	(b) cellulose acetate
a =	10,1 Å.U.	9,2 Å.U.
b =	8,6 Å.U.	7,1 Å.U.
c =	10,8 Å.U.	9,8 Å.U.

Hence v = 935 cubic Å.U. and v = 636 cubic Å.U. for (a) and (b) respectively.

It is evident, that the values differ but little from each other and from those found for untreated cellulose. (see p. 460). *This is obviously the fundamental condition for the possibility of a topochemical reaction.*

Fibres obtained from a denitrated cellulose nitrate and from a saponified cellulose acetate, both nitrate and acetate originally prepared from untreated cellulose, yield the diagram of the untreated cellulose, while the corresponding fibres obtained from mercerised fibres, instead of untreated cotton, show the diagram of mercerised cellulose (cellulose hydrate). In spite of this remarkable result, decisive conclusions cannot as yet be drawn as to whether the change produced by mercerisation is to be interpreted from a 'chemical' or 'physical' point of view.

The lengths of the edge of the crystallites of cellulose nitrate appear to be 100 and 58; of cellulose acetate 111 and 61 Å.U., that is about the same value as found for cellulose.

PART II

Effect of Previous Treatment on the Size of Particles of Dissolved Cellulose Nitrate

(Carried out with D. Krüger).

It has long been recognized and was pointed out in Part I, of the present communication, that the nitration of cellulose fibres can easily be carried out in such a way that the fibrous structure remains unchanged. From various experiments it seemed probable that these and other chemical transformations of cellulose actually take place within the structural unit of each crystallite, partly without alteration in the mutual arrangement of the crystallites. It has been shown in Part I that in spite of chemical interaction, neither the dimensions of the unit-cell nor those of the crystallites are markedly changed. It is of equal importance to show that in colloidal dispersions the *size of particles is identical with that of the original crystallites.* It follows from this that primarily, the process of dispersion consists only in a separation of the crystallites.

---

[1] Kolloid-Z., **18**, 99, 222 (1916); **20**, 173 (1917): Z. Mikrosk., **32**, 43 (1915); Nachr. Göttingen ges. math.-phys. Kl. (1919).

[2] Dissertation. Jena (1914).

[3] Ber., **57**, 329, 750 (1924); E Möhring: Wiss. und Ind., **2**, 70 (1923).

A large number of celluloses of different origin and pre-treatment have been carefully nitrated, washed, dried, etc., and then dissolved in acetone or other solvents, the influence of the "process of dissolving" being studied separately.

The determination of the size of the particles in colloidal solution was carried out by free diffusion into the solvent.

The diameters of the particles, which may be approximately regarded as spheres, were calculated on the one hand from the formula given by Einstein[1]; on the other hand from the semi-empirical relation $M\sqrt{D} = 7$. (M = molecular weight; D = coefficient of diffusion in aqueous solution at 20°C)[2], the observed D being corrected for 20°C and converted to the value for aqueous solutions by means of the ratio of the viscosities of the solvent actually used to that of pure water.

The calculation of the diameter of the particles is based on the assumption of spherical particles and accomplished by the customary procedure from Avogadro's number N.

In Table VI, D is the coefficient of diffusion determined at 13°C, $2\rho_1$ and $2\rho_2$ the diameters computed according to Einstein's law and from the square root relation, respectively.

The table shows that with products of different origin, the size of particles is approximately of the same order, a conclusion based on the dimensions of the crystallites in the fibre.

Further it follows that a short grinding of cellulose in the beating-engine brings about a considerable reduction in the size of particles in the solution of cellulose nitrate.

The treatment of cellulose with reagents such as strong acid or alkali, results in a decreased size of particles in the solution of cellulose nitrate. The size of particles, as found in the case of viscose silk after nitration, corresponds approximately to the reduction in size, which takes place during the "dreripening" in the manufacture of viscose silk, i.e. the mercerisation process.

The values of $2\rho_1$ found are about 2 to 3 times those of $2\rho_2$. If the $2\rho_2$-value of the dissolved cellulose nitrate from hemp is compared with those calculated from the breadth of the interference blackening of hemp fibre and nitrated

---

[1] Ann. Phys., (4) **19**, 303 (1906).

[2] L. W. Oeholm: Medd. Vetenskaps. Nobel-Institut, **2**, Nr. 23 (1912).

TABLE VI

Size of particles of cellulose nitrate prepared from various celluloses.

Material		Solvent	D	$2\rho_1$[1]	$2\rho_2$[1]
cotton	(as nitrate)	acetone	0,035	300 Å.U.	94 Å.U.
”	”	methylethyl-keytone	0,023	340 ”	
hemp	”	”	0,039	200 ”	74 ”
ramie	”	”	0,042	186 ”	66 ”
flax	”	”	0,043	182 ”	66 ”
sulphite-cellulose	”	”	0,045	174 ”	64 ”
viscose silk	”	”	0,053	148 ”	56 ”
hemp, ground 25 min. in the beating-engine	”	”	0,075	104 ”	44 ”
cotton, mercerised 3-4 hrs.	”	”	0,043	182 ”	66 ”
cotton, mercerised 70 hrs.	”	”	0,085	88 ”	41 ”
cotton, treated with 50% H_2SO_4 2 hrs. at room temperature	”	”	0,039	200 ”	68 ”
cotton, treated with 50% H_2SO_4 20 hrs. at room temperature	”	”	0,059	132 ”	52 ”

hemp cellulose, the agreement is strikingly good, as is shown by the following table:

Dimensions of crystallites of hemp fibre: 117 and 66 Å.U.

Dimensions of crystallites of cellulose nitrate from hemp (solid state): 100 and 58 Å.U.

Diameter of colloidal particles of nitrated hemp fibre (dissolved) 74 Å.U.

This result shows, as stated above, that the chemcial transformation is accomplished within the complex of atoms united in the crystallite, without the latter undergoing disintegration to single ($C_6H_{10}O_5$) groups, and is thus in complete agreement with the results of X-ray analysis. *It is thus possible, from the dimensions of colloidal particles as found in solutions of cellulose nitrate to determine the size of the original crystallites of cellulose.*

---

[1] In order to make the diameters of particles of cellulose nitrate and the length of crystallites of cellulose directly comparable with each other, the values of $2\rho_1$ and $2\rho_2$ quoted above are to be divided by $\sqrt[3]{\frac{M_1V_1}{M_2V_2}} = 1,2$. ($M_1$, M_2 and V_1, V_2 denoting the molecular weight and the molecular volume of cellulose nitrate and of cellulose, respectively.

Summary

1. The results of the Röntgenspectrographic investigation of cellulose are given, and the observed values compared with those calculated from the quadratic equation for rhombic symmetry, assuming the unit-cell to consist of four ($C_6H_{10}O_5$) groups.

It is shown that rhombic symmetry and the adopted size of unit-cell are in better agreement with the experimental data than any other assumption.

2. The quadratic equation for mercerised cellulose is given.

3. The dimensions of crystallites of natural cellulose fibres have been determined.

4. It is shown that the behavior of bast fibres in both the magnetic and the electric field runs completely parallel to the results of optical measurements and X-ray investigations.

5. The X-ray investigation of cellulose nitrate and cellulose acetate indicates that the dimensions of these derivatives differ but little from those of the original untreated cellulose.

It has been pointed out that this fact is a necessary condition for assuming a topochemical reaction.

6. Cellulose fibres obtained by the denitration of a cellulose nitrate and from the hydrolysis of a cellulose acetate (both of them being prepared from an untreated cellulose) give the diagram of the latter. On the other hand, cellulose regenerated from esters prepared from a mercerised cotton give the diagram of cellulose hydrate.

7. The dimensions of the crystallites of nitrated and acetylated hemp cellulose are given, the esterification being carried out as carefully as possible, and under conditions in which the fibrous structure is maintained.

8. *The size of particles in colloidal solutions of cellulose nitrate as determined by the diffusion method corresponds exactly to the dimension of crystallites, computed from the X-ray diagram.*

9. The size of particles of cellulose of various origin and pre-treatment is given.

THE THERMAL DECOMPOSITION OF FORMIC ACID

BY WM. L. NELSON AND CARL J. ENGELDER

In some investigations on formic acid recently carried out in this laboratory, it became necessary to study the thermal decomposition of this acid without the intentional addition of catalysts, in reaction tubes of various materials, over a temperature range from 250° to 550°C. Formic acid in its decomposition is so sensitive to catalytic influence that it was to be expected that the walls of the reacting vessel would reveal a specific effect and largely influence the course of the reaction. More extensive studies of this kind have recently been reported by Hinshelwood and his co-workers, who studied the decomposition in bulbs of various glasses and with platinum, palladium, silver, and titanium dioxide as catalysts at temperatures up to 350°C. Reference to their work will be made later. Muller and Peytral[1] passed the vapors of formic acid through a small platinum tube at 1150°C and concluded that the primary decomposition was into CO_2 and H_2.

Experimental

The apparatus used in the experiments here recorded was substantially the same as that used in catalytic work of this kind. The vapor of formic acid was passed through the various tubes inserted in the hollow core of an electrically heated furnace, the liquid products condensed, and the gases collected over a saturated salt solution on top of which was a layer of heavy paraffin oil.

The formic acid, prepared by three vacuum distillations of 85% acid over anhydrous copper sulfate, was practically anhydrous, and had a specific gravity of 1.22. The flow of acid through the reaction tubes, accurately controlled by the method of displacement by mercury[2], was maintained uniformly at the rate of three cc. per hour. The acid was vaporized in a preheater maintained at a temperature somewhat above the boiling point of the acid.

The furnace was built upon a grooved silica tube, 24″ long and 1″ diameter, wound with nichrome wire and insulated with alundum and kieselguhr. The furnace was maintained at the desired temperatures by means of a Leeds and Northrup Thermo-Regulator. The reaction tubes were 30″ long and about 1″ external diameter and fitted snugly into the core of the furnace. The thermo-couple, cased in a pyrex tube, penetrated half way into the reaction tube.

Beginning at 350°C., the gaseous decomposition products were analyzed over mercury with the Hempel apparatus immediately after runs. In general, CO_2 was determined by absorption in potassium hydroxide and H_2 and CO were determined by slow combustion over mercury. Occasionally, when it seemed desirable to check up on the presence of hydrocarbons, the CO was determined by absorption in acid cuprous chloride, and the residual gas analyzed for hydrogen and hydrocarbons by slow combustion. Only fractional percentages of saturated hydrocarbons, presumably methane, were ever found, so that it was deemed sufficiently accurate to determine, in general, only CO_2, CO, and H_2. The apparatus was always flushed by making a run of about one hour's duration before collecting and analyzing the gas mixture, yet traces of air were present, so that all analyses and volumes recorded below have been calculated to an air-free basis and corrected to N.T.P.

---

[1] Muller and Peytral: Bull., **29**, 34 (1921).

[2] Adkins and Nissen: J. Am. Chem. Soc., **46**, 140 (1924).

Results

Representative samples of gas were analyzed for the runs at the temperatures indicated in the tables. In all cases, 3 cc. of formic acid was vaporized and passed through the reaction tube per hour. The analyses of the gas mixtures, together with the volume of gas at N.T.P. and the volumes of CO_2, H_2, and CO resulting from the decomposition of one cubic centimeter of liquid formic acid are here recorded for tubes of pyrex glass, unglazed porcelain, unetched and etched silica, and copper.

Pyrex Glass Tube

Decomposition became evident at 250°C, yielding 10 cc. of gas per cc. acid. At 300°C the gas evolution reached 40 cc. per cc. acid.

°C	Composition of Gas Mixture			1 cc. Formic Acid yielded:			
	% CO_2	% H_2	% CO	cc. Total	cc.CO_2	cc.H_2	cc.CO
350	49.1	49.1	1.8	270	132.6	132.6	4.8
400	49.6	48.0	2.4	580	287.7	278.4	13.9
500	45.3	40.3	14.4	750	339.7	302.2	108.0
600	42.5	39.4	18.1	910	386.7	358.5	164.7

Unglazed Porcelain Tube

At 250°C. the gas evolution was 30 cc. and at 300°C it was 50 cc. per cc. acid.

°C	Composition of Gas Mixture			1 cc. Formic Acid yielded:			
	% CO_2	% H_2	% CO	cc. Total	cc.CO_2	cc.H_2	cc.CO
350	49.0	48.7	2.3	440	215.6	214.3	10.1
450	53.4	43.9	2.7	910	485.9	399.5	24.6
550	53.2	36.9	9.9	800	425.6	295.2	79.2

Unetched Silica Tube

The gas yield at 250°C was 30 cc. and at 300°C, 120 cc. per cc. acid.

°C	Composition of Gas Mixture			1 cc. Formic Acid yielded:			
	% CO_2	% H_2	% CO	cc. Total	cc.CO_2	cc.H_2	cc.CO
350	50.0	48.4	1.6	730	365.0	353.3	11.7
450	51.3	47.1	1.6	980	502.7	461.6	15.7
550	50.8	45.6	3.6	950	482.6	432.2	34.2

Etched Silica Tube

The above tube was rather deeply etched with hydrofluoric acid and then used as reaction tube. Decomposition was the same at 250°C as with the unetched tube, but at 300°C the gas evolution reached 400 cc. per cc. acid.

°C	Composition of Gas Mixture			1 cc. Formic Acid yielded:			
	% CO_2	% H_2	% CO	cc. Total	cc.CO_2	cc.H_2	cc.CO
350	50.2	49.5	0.3	940	471.9	465.3	2.8
450	51.1	47.5	1.4	1010	516.1	479.7	14.1
550	50.0	42.2	7.8	900	450.0	379.8	70.2

Copper Tube

°C	Composition of Gas Mixture			1 cc. Formic Acid yielded:			
	% CO_2	% H_2	% CO	cc. Total	cc.CO_2	cc.H_2	cc.CO
300	—	—	—	110	—	—	—
350	48.7	47.8	3.5	360	175.3	172.0	12.6
450	49.7	49.9	0.4	1120	556.6	558.9	4.5
550	49.7	49.9	0.4	1130	561.6	563.9	4.5

Discussion of Results

Sabatier and Mailhe[1], Hinshelwood[2] and others, and Adkins[3] have shown that formic acid undergoes decomposition according to one or more of the three primary reactions:—

$$(1)\quad HCOOH = CO_2 + H_2$$
$$(2)\quad HCOOH = CO + H_2O$$
$$(3)\quad 2HCOOH = CO_2 + H_2O + HCHO$$

the extent on each depending on the specific nature of the catalyst and the character of the reaction vessel.

In addition, over the temperature range covered here the decomposition of formaldehyde, according to the reaction:—

$$(4)\quad HCHO = H_2 + CO$$

must be taken into account.

Consideration of these four reactions shows that the CO_2 found may be accounted for by reactions (1) and (3); that the H_2 may have its origin in reactions (1) and (4), and that the CO may arise from reactions (2) and (4). That reaction (3) takes place to some extent is shown by the excess of the volume of CO_2 over that of H_2 and by the further fact that formaldehyde was found in the condensate of all runs at the lower temperatures. The thermal decomposition of formaldehyde according to reaction (4) has been studied by Bone and Smith[4] and more recently by Hofmann and Schibsted[5]. The more or less complete dissociation into H_2 and CO of the formaldehyde formed will contribute its quota of these gases to those arising from the direct decomposition of formic acid itself.

---

[1] Sabatier and Mailhe: Compt. rend., **152**, 1212 (1911).

[2] Hinshelwood, Hartley and Topley: Proc. Roy. Soc., **100A**, 575 (1922); Tingley and Hinshelwood: J. Chem. Soc., **121**, 1668 (1922); Hinshelwood and Topley: **123**, 1014; Hinshelwood and Hartley: 1333 (1923).

[3] Adkins: J. Am. Chem. Soc., **45**, 809 (1923).

[4] Bone and Smith: J. Chem. Soc., **87**, 910 (1905).

[5] Hofmann and Schibsted: Ber., **51**, 1398 (1918).

Turning to the data, inspection shows that by far the greater amount of gas (H_2 and CO_2) is produced by reaction (1). The consistent excess of CO_2 over that of H_2 must be attributed to reaction (3). This is substantiated by the finding of formaldehyde in the condensate. The volume of carbon monoxide shows a steady increase with rise in temperature for all tubes except that of copper. Its presence can be accounted for by the direct decomposition of formic acid according to reaction (2), which according to Hinshelwood takes place to an equal extent with reaction (1) at 280°C, and is the reaction that takes place almost exclusively at low temperatures in the presence of titanium oxide as catalyst, an observation first made by Sabatier and later confirmed by Hinshelwood and by Adkins. On the other hand, it is equally possible to account for the CO through the secondary decomposition of formaldehyde according to reaction (4), a reaction which does take place to a certain extent. This latter supposition is as consistent with our data as the former, so one cannot say with certainty which of these two reactions is the one yielding the CO. Probably both are involved.

Obviously, with the data at hand, bearing in mind that each of these gases may arise from at least two separate reactions, no exact calculation can be made of the extent to which each reaction proceeds under the conditions of the experiment. Tentative calculations based on the gaseous products have, however, been made of the amount of decomposition undergone by the acid in its passage through the tubes at the rate of 3 cc. per hour, and of the extent to which each primary reaction is influenced.

In the first set of such tentative calculations, the decomposition has been based on reactions (1), (2), and (3), not taking into separate account the amounts of CO and H_2 which come from the partial decomposition of formaldehyde. The total H_2 found is thus a measure of reaction (1), the total CO a measure of reaction (2), and the excess of CO_2 over that of H_2 a measure of reaction (3). If one cc. of liquid formic acid decomposes completely according to (1), there should result 1186 cc. of gas, consisting of equal volumes of CO_2 and H_2; if according to reaction (2), 593 cc. of pure CO; if according to (3), 296 cc. of CO_2, assuming here no decomposition of the HCHO. In this way the extent to which one cc. of acid was decomposed in the direction of (1), (2), and (3) was computed, the total percentage decomposition being the sum of all three. Thus, for example, for the unetched silica tube at 350°C, 59.4% of the acid passed through decomposed according to (1); 2.0% according to (2); and 4.0% according to (3); giving a total decomposition of 65.4%. The extent to which the three modes of decomposition are divided among themselves gives a better approximate idea of the course of these reactions. In the above example, for every 100 molecules decomposed, 90.8 follow reaction (1), 3.0 follow reaction (2), and 6.2 follow reaction (3). Typical results computed by this method are given in the table below for the etched and unetched silica tube. These figures can only be taken as approximations, but they are useful in showing the differences obtainable with smooth and rough surfaces of the same material.

In another tentative method of calculation, the decomposition has been based on reactions (1) and (3), assuming that all the CO and an equal volume of H_2 have been derived from the secondary partial decomposition of the formaldehyde formed in reaction (3). The apparent extent to which reaction (1) proceeds can then be taken as the total H_2 formed, less a volume equal to that of the CO found. The excess of CO_2, as a measure of (3), will thus be somewhat larger than by the first method of computation. The volume of CO gives a measure of the gaseous decomposition of formaldehyde; the CO_2 attributed to reaction (3) is always in excess of the CO indicating that the formaldehyde does not decompose completely into gaseous products, but forms the oily and tarry polymerization products found in the condensate. The data for the tubes have been calculated in this manner and compared with the first method. The results for the two silica tubes are given below.

Unetched Silica Tube

°C	Total % Decomp.	Method 1 Extent followed by reaction per 100 molecules decomposed (1)	(2)	(3)	Method 2 Extent followed by reaction per 100 molecules decomposed (1)	(3)
350	65.4	90.8	3.0	6.2	87.9	12.1
450	94.3	82.5	2.8	14.7	79.8	20.2
550	95.7	76.2	6.1	17.7	70.1	29.9

Etched Silica Tube

°C	Total % Decomp.	Method 1 Extent followed by reaction per 100 molecules decomposed (1)	(2)	(3)	Method 2 Extent followed by reaction per 100 molecules decomposed (1)	(3)
350	81.2	96.7	0.6	2.7	96.0	4.0
450	95.6	84.7	2.5	12.9	79.0	21.0
550	99.6	64.3	11.9	23.8	52.5	47.5

Comparable results were obtained with the other tubes. In the case of the porcelain tube at 550°, the abnormally large excess of CO_2 gives an apparent total decomposition of over one hundred percent; either the data for this run are at fault, or the inadequacy of this tentative method of calculation is here revealed. The slight deficiency of CO_2 for the copper tube at the higher temperatures is well within the limits of error of the gas analysis.

Obviously, such calculations are only approximations and sweeping conclusions cannot be drawn from them. The matter becomes still more complicated when one considers the possibility of secondary reactions taking place, such as the reduction of carbon dioxide by hydrogen and the formation of methyl alcohol. The reaction:—

$$(5)\quad CO_2 + H_2 \longrightarrow CO + H_2O$$

according to Muller and Peytral accounts for the presence of CO at 1150°C, these investigators concluding that the only primary reaction in the decomposition of formic acid at this high temperature is the one giving CO_2 and H_2. To what extent this reduction takes place over the temperature range covered has not been investigated by us. In some cases, equilibrium concentrations for the water gas equilibrium are reached, as shown by calculations of the equilibrium constant $CO \times H_2O/CO_2 \times H_2 = k$, yet no definite conclusions can be drawn from the data available here. This point requires more investigation.

Conclusions

Formic acid when slowly passed through tubes of silica, pyrex, porcelain, and copper, heated to temperatures of from 350° to 550°C, decomposes principally into CO_2 and H_2, according to the reaction:—

$$HCOOH = CO_2 + H_2$$

A certain, usually small, amount decomposes according to the reaction:—

$$2HCOOH = CO_2 + H_2O + HCHO$$

The two reactions:—

$$HCOOH = CO + H_2O$$
$$HCHO = CO + H_2$$

account for the CO found.

The decomposition is 90% or more complete at 450°C. The pyrex glass tube is least active; the copper tube most active. The silica tube after being etched shows a much greater activity than it did in its unetched condition, showing the effect of increased active surface. With the copper tube reaction (1) takes place almost exclusively and brings about a decomposition of over 99% at 450° and 550°C.

No exact calculation can be made of the extent to which each reaction proceeds on account of the complications arising in the gas volume relationships.

The instability and sensitiveness of formic acid to the catalytic influence of the walls of the reacting tube are shown by the results here recorded. These results have an important bearing on the work of Wescott reported in the next paper.

University of Pittsburgh,
Pittsburgh, Pa.
December, 1925.

THE CATALYTIC DECOMPOSITION OF FORMIC ACID

BY B. B. WESCOTT AND CARL J. ENGELDER

The experiments of Nelson, reported in the preceding paper, have shown that when formic acid is slowly passed through tubes of various materials heated to temperatures of 350° to 550°C, the decomposition is mainly in the direction of CO_2 and H_2, according to the reaction:—

$$(1)\quad HCOOH = CO_2 + H_2$$

The excess of CO_2 over H_2, together with the production of formaldehyde shows that the following reaction takes place to a certain extent:—

$$(3)\quad 2HCOOH = CO_2 + H_2O + HCHO$$

The decomposition of formaldehyde into CO and H_2 at these temperatures accounts for at least some of the CO and H_2 found in the gaseous decomposition products.

The dehydration of formic acid according to the reaction:—

$$(2)\quad HCOOH = CO + H_2O$$

undoubtedly takes place to some extent.

That these reactions are greatly influenced by dehydrating and dehydrogenating catalysts is well known from the work of Sabatier[1] and the recently published papers of Hinshelwood[2] and Adkins[3]. These investigators worked at temperatures up to 350°C. The former used a layer of catalyst 50 cm. long, heated in a Jena glass tube. Hinshelwood employed bulbs coated with the metallic catalyst or partly filled with the powdered material. The effect produced by relatively small amounts of alumina, titania and nickel as catalysts on the decomposition of formic acid over a temperature range from 200° to 500°C has been studied by Wescott and recorded in the present paper. The extent to which the wall reactions have been modified by the insertion of the catalysts is shown by the data here presented.

Experimental Procedure

The apparatus consisted of a burette for measuring the acid used, a vaporizer, an electrically heated and controlled furnace containing the reaction tube, a suitable condensing train, and a gas collection vessel. The acid was practically anhydrous, obtained from Kahlbaum's and from Merck's. The acid was admitted at a uniform rate of about 10 cc. per hour. The gaseous products were analyzed by the usual methods of gas analysis. The undecomposed formic acid and formaldehyde were removed in the condensing train.

The reaction tube was an unglazed clay Johnson combustion tube such as used in steel mill laboratories for carbon determinations. It was 40 cm. long and about one and a half cm. internal diameter. It decomposed formic acid, when passed through it at the rate of 10 cc. per hour, mainly into H_2 and CO_2.

---

[1] Sabatier and Mailhe: Compt. rend., **152**, 1212 (1911).

[2] Hinshelwood and Topley: J. Chem. Soc., **123**, 1014 (1923).

[3] Adkins: J. Am. Chem. Soc., **45**, 809 (1923).

The decomposition became apparent at 294°C yielding 7cc. gas per cc. acid. At 400° the gas evolution reached 320 cc. gas per cc. acid, of which 166.7 cc. were CO_2, 163.3cc. H_2, and 14.7 cc. CO. At 484° the gas yield was 274.7 cc. CO_2, 271.6 cc. H_2, and 36.7 cc. CO, or a total of 582 cc. per cc. acid. These values are lower than those obtained by Nelson with other tubes at a slower rate of passage but they are similar in general characteristics.

To get the superimposed effect of the catalysts, these were spread in a thin layer in a combustion boat about 10 cm. long and placed in the middle of the tube.

Titania Catalyst

A sample of ignited titanium dioxide ground to pass a 200-mesh sieve when used in a shallow layer about 10 cc. long gave the results shown in Table I. Another sample made by precipitation from titanium tetrachloride yielded similar results.

TABLE I

1 cc. Formic Acid yielded:

°C	cc. Total Gas	cc. CO_2	cc. H_2	cc. CO
202	38.8	2.7	1.8	33.7
234	63.4	4.9	3.8	54.6
280	177.6	19.5	16.0	142.
340	439.0	128.	112.3	197.
375	657.0	241.	222.0	189.
398	820.0	274.	246.	293.
498	777.5	248.	211.	308.

Alumina Catalyst

The alumina catalysts were prepared in general by dissolving aluminum sulfate in water, largely diluting, and precipitating the aluminum hydroxide with dilute ammonium hydroxide. The precipitate was washed several times by decantation, filtered, dried at 250° and ground to pass a 200-mesh sieve. Portions of the dried Al_2O_3 from the same preparation were used in the series of temperature runs. The results of a typical series of runs are given in Table II. These results as well as those with titania have been confirmed in a general way by another student, Mr. E. H. Ohl, working in the same laboratory.

TABLE II

1 cc. Formic Acid yielded:

°C	cc. Total Gas	cc. CO_2	cc. H_2	cc. CO
287	178.	9.4	6.0	164.0
311	243.	12.4	10.5	223.
338	422.5	91.2	85.0	242.
373	619.0	215.5	199.	205.
417	850.0	300.	287.	259.
491	763.0	221.	189.	354.
503	754.5	214.	183.	354.

Nickel Catalyst

The nickel catalysts were prepared by ignition of the nitrate to the oxide followed by reduction to the finely divided metallic form in a stream of hydrogen in a separate furnace and subsequently transferred as needed to the catalytic apparatus without contact to the air. The results are given in Table III.

TABLE III

1 cc. Formic Acid yielded:

°C	cc. Total Gas	cc. CO_2	cc. H_2	cc. CO
210	327.	157.6	152.	18.6
257	490.	235.	220.5	34.6
353	873.	453.	395.5	36.7
455	814.	365.	311.	138.
524	801.	283.	257.	262.

Discussion of Results

The results show that with titania and alumina the dehydrating reaction ($HCOOH = CO + H_2O$) greatly predominates up to temperatures somewhat above 300°C, reactions (1) and (3) being of minor importance. This is what would be expected of these dehydrating catalysts and the results confirm in general the work of earlier investigators. With nickel, the dehydrogenating reaction ($HCOOH = CO_2 + H_2$) takes place almost exclusively at the lower temperatures, as indicated by the large volume of CO_2 and H_2 evolved, reactions (2) and (3) taking place to a minor extent. That these minor reactions with all three catalysts are not solely the effects of the tube can be deduced from the blank runs made under otherwise identical conditions and from Nelson's data on other tubes where the wall decompositions were studied under more nearly equilibrium conditions.

At the higher temperatures the course of the main reaction is more difficult to follow and the volume relationships become complicated. With the titania catalyst at 340° reaction (2) comes to the front, accounting for about 51% of the gas yield; at 398° it accounts for about 63% of the total gas evolved. This reaction is the one taking place selectively at the walls of the tube but the wall reaction accounts for only about one-half the amounts of CO_2 and H_2 found here, hence the titania itself catalyzes this reaction to some extent as well.

The alumina catalyst, like TiO_2, catalyzes the dehydrating reaction almost exclusively at lower temperatures. At 373° the dehydrogenating reaction becomes of equal importance. At the highest temperatures observed, 491° and 503°C, the CO production is again in excess of that of CO_2 and H_2. Adkins[1] found that the extent to which these two reactions are selectively catalyzed depends upon the method of preparation of the alumina catalysts.

---

[1] Adkins: J. Am. Chem. Soc., **45**, 809 (1923).

The abnormally large amounts of CO found in the nickel runs at 455° and 524° are difficult to account for. It seems unlikely that the primary decomposition of the acid into CO and H_2O should show this sudden increase at these temperatures with nickel as catalyst. The tube reaction at these temperatures follows this direction to only a minor extent. Formaldehyde, decomposing into CO and H_2, cannot yield these large amounts of CO consistently with the other data. The possibility of nickel catalyzing the reaction:

$$(5)\quad CO_2 + H_2 \longrightarrow CO + H_2O$$

presents itself. This reduction of CO_2 by H_2 was noted by Sabatier and Senderens[1] for an active copper catalyst, but with nickel, hydrogenation to methane is the usual result:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

With the nickel used by Wescott, no methane was found. The corresponding decrease in the volumes of H_2 and CO_2 favor this explanation. The effect of active metal catalysts on the water gas equilibrium is under investigation and may throw light on the results here presented.

Reaction (3) takes place to a small extent in all the runs and can be attributed solely to the effect of the walls of the tube.

The extent to which the primary decompositions are influenced by the introduction of the catalysts is readily seen at the lower temperatures. The wall-reactions and secondary effects partly obscure the specific catalytic effect at higher temperatures. Calculations based on the effect of the catalysts would, therefore, be misleading.

Conclusions

The catalytic effect of small amounts of alumina, titania, and nickel on the decomposition of formic acid between 200° and 500°C has been studied. The reactions taking place at the walls of the reaction tube have been greatly modified through the presence of added catalysts. Alumina and titania catalyze the dehydration reaction:—

$$HCOOH = CO_2 + H_2$$

The tube itself decomposes the acid chiefly according to this reaction, with the dehydrating reaction and the reaction:

$$2HCOOH = CO_2 + H_2O + HCHO$$

playing minor roles. Formaldehyde decomposes partially into H_2 and CO. The effect of the tube becomes marked above 350°.

University of Pittsburgh,
Pittsburgh, Pa.
December, 1925.

---

[1] Sabatier and Senderens: Ann. Chim. Phys. (8), **4**, 426 (1905).

INFLUENCE OF TEMPERATURE ON METABOLISM AND THE PROBLEM OF ACCLIMATIZATION

BY N. R. DHAR

It is well known that the temperature of a warm-blooded animal is maintained at the normal even though the temperatures of the outside environments vary from zero and lower to 30° or 35°. In cold-blooded animals, on the other hand, the temperature of the body is only slightly higher than that of the environment at the time. The metabolism of such animals varies with the temperatures in such a manner that the respiratory exchange almost always rises with the increase in temperature, but generally irregularly and to a very different degree in different animals. The frog in the mud during the winter at a temperature of 4° has quite a different metabolism from that which he enjoys during the summer sunshine as it sits on the river bank and snaps at passing flies.

Röhrig and Zuntz[1] first showed that a curarized warm-blooded animal at ordinary room temperatures lost the power of maintaining its body temperature and that the intensity of metabolism decreased accordingly. Curare prevents the transmission of motor impulses to voluntary muscles. Krogh[2] states that the curve of oxygen absorption as influenced by body temperature is the same in the anesthetized frog and fish as in the curarized dog. In warm-blooded animals the temperature is maintained at a constant level independent of the climatic condition and this level is a favorable one for the activity of nerve and muscle. It would indeed be inconvenient were the active life of a man dependent upon the temperature of the environment. The essential mechanism for the regulation of body temperature is nervous.

In warm-blooded animals a fall in the surrounding temperatures regularly causes not a decrease but an increase in the respiratory exchange, thanks to the mechanism of chemical heat regulation. The most elaborate study of the chemical heat regulation has been made by Rubner[3] who obtained the results given in Table I in the case of a guinea pig.

TABLE I

Temperature of air °C.	CO_2 per Kg. and Hour Gr.
0°	2.91
11°	2.15
21°	1.77
26°	1.54
30°	1.32
35°	1.27
40°	1.45

---

[1] Pflüger's Archiv, 4, 57 (1871).

[2] Internat. Z. physik-chem. Biologie, 1, 492 (1914).

[3] "Die Gesetze des Energieverbrauchs bei der Ernährung" (1902).

At 35° the regulation breaks down and the respiratory exchange rises with increase in temperature of the body as seen in the last experiment of the above series.

In the foregoing paper[1] we have shown that under standard conditions where the effect of nervous influence is excluded increase in temperature causes greater metabolism in both warm and cold blooded animals.

After studying a considerable range of animals, Rubner has found that all animals transform nearly the same total amount of energy per kilogram of body weight in the whole period from the birth to the natural death. The mean value of the constant Rubner finds to be 191600 calories, the values for different species ranging from 141091 and 265500 calories. Small animals with an intensive metabolism live a relatively short time; large animals with more sluggish metabolism live a longer time. Rubner's view is that a definite sum of living action or energy transformation determines the physiological end of life. It is Rubner's law that the metabolism is proportional to the superficial area of an animal.

Erwin Voit[2] has calculated the following results, Table II, for showing the heat production in resisting animals of various sizes at medium temperatures of the environment:—

TABLE II

	Weight in Kg.	Calories produced	
		Per Kilo	per Sq. M. Surface
Horse	441	11.3	948
Pig	128	19.1	1078
Man	68.3	32.1	1042
Dog	15.2	51.5	1039
Rabbit	2.3	75.1	776
Goose	3.5	66.7	969
Fowl	2.0	71.0	943
Mouse	0.018	212.0	1188
Rabbit (without ears)	2.3	75.1	917

This table supports the generalization of Rubner.

Voit shows that the metabolism of the pigeon may be doubled after removing its feathers. From the experiments of Rubner it appears that the presence of adipose tissue acts in the same way as does a warm fur to extend the range of the physical regulation and to delay the onset of chemical regulation of body temperature. That the range of physical regulation of temperature of a small dog was due to his long hair, is shown by the change in his metabolism after shaving him. Rubner shows this in Table III.

---

[1] Dhar: Proc. Akad. Wet. Amsterdam, 23, 44 (1920).

[2] Z. Biologie, 41, 120 (1907).

TABLE III

Temperature	Calories per Kilo. Normal coat of hair	Calories per Kilo. Shaved
20°	55.9	82.3
25°	54.2	61.2
30°	56.2	52.0

It is clearly seen that this dog lost its power of physical regulation between 20° and 30°. As soon as he lost his covering of hair his metabolism became like that of a guinea pig, increasing with a reduction of temperature from 30° downwards, an illustration of chemical regulation.

To determine the influence of the protective layer of fat Rubner investigated the influence of temperature on the metabolism of a fasting short haired dog at a time when he was emaciated and compared it with the fasting metabolism after the same dog had been fattened, Table IV.

TABLE IV

Dog (thin)		Same dog (fat)	
Temperature	Cal. per Kilo.	Temperature	Cal. per Kilo.
5.1°	121.3	7.3°	120.5
14.4°	100.9	15.5°	83.0
23.3°	70.7	22.0°	67.0
30.6°	62.0	31.0°	64.5

It appears from this table that the metabolism of the dog was the same at a low temperature in both cases but that the minimum metabolism was almost reached at a temperature of 22° when the dog had a protective covering of fat which was not the case when he was thin.

The physical regulation may be increased by certain voluntary acts, such as are observed when a dog or man exposed to cold lies down and curls himself up in such a way as to offer as small an exposed surface as possible. The contrast to this is offered when on a hot day the dog lies on his back and extends his legs so as to promote loss of heat.

In Table V are Voit's results on the effect of temperature on the metabolism of a fasting man (six hour periods.)

TABLE V

Temperature	CO_2 excreted in grams	Temperature	CO_2 excreted in grams
4.4°	201.7	23.7°	164.8
6.5°	206.0	24.2°	166.5
9.0°	192.0	26.7°	160.0
14.3°	155.1	30.0°	170.6
16.2°	158.3		

Voit believed the increase in metabolism to be a reflex stimulus of cold on the skin which raised the power of muscle cells to metabolise.

Another factor in the heat regulation of man is clothes. Certain savage races living in cool climates do without clothes, as, for example, aborigines of Tierra del Fuego, who according to the reports of travellers, substituted a covering of oil. In such races the process of "hardening" or development of physical regulation must be carried to a maximum. In civilized countries man endeavors to remove all the influence of chemical regulation by keeping his skin covered. Only about 20% of his surface is normally exposed to the air. The most important constituent of clothes is the air, which is a much worse conductor of heat than is fibre. Two experiments cited by Rubner indicate the effect of clothes on metabolism. An individual was kept at a temperature of between 11° and 12° and wore different clothes at different times. His CO_2 and water excretion are given in Table VI.

TABLE VI

Influence of Clothes on Metabolism in Man at a Temperature of 11° to 12°

	CO_2 in gram. per hour.	Remarks
Summer clothes	28.4	Cold, occasional shivering
Summer clothes and winter overcoat.	26.9	Chilly part of the time.
Summer clothes and fur coats.	23.6	Comfortably warm.

When a man was comfortable the chemical regulation of temperature was eliminated.

Fat persons have been directly observed to have a smaller respiratory action than lean ones. Benedict and Smith[1] have shown by comparing a number of athletes with normal subjects of similar heights and weights that the metabolism of athletes is on the average distinctly greater than that of non-athletes.

While it had often been observed that smaller animals had per unit weight a greater respiratory exchange than larger ones, a quantitative study of the influence of size upon metabolism was first made by Rubner on grown dogs weighing from 30.4 to 3.4 kilograms. Rubner found that the metabolism calculated per kilogram increases regularly with decreasing size. When however the surface of the animal is taken into account a practically constant metabolism per sq. surface was found for all.

From experiments on guinea pigs of different age and weights Kettner[2] finds that the metabolism per kilogram an hour decreases fairly regularly with increasing weight whilst the differences in the results per sq. meter are independent of size. On the other hand, in a recent discussion Benedict[3] denies that there is any close relationship between size and metabolism and deprecates especially the use of the surface as a basis for comparison. His own figures and charts show, however, that such relationships exist that the metabolism per kg. of the body weight decreases fairly regularly with increasing weight.

---

[1] J. Biol. Chem., **20**, 243 (1915).

[2] Archiv Physiol., **1909**, 447.

[3] J. Biol. Chem., **20**, 263 (1915).

The surface S of an animal is approximately proportional to the square of a linear dimension e.g. length of the body, while the weight is proportional to the third power of a linear dimension. We have therefore $S = CW^{\frac{2}{3}}$ the constant C has been worked out for different species. It does not vary very much even in forms of very different shapes. For man and also for a dog we have C = 12.3 for the rabbit 12.9, the horse 9.0, the rat 9.1 and the guinea pig 8.9.

It is quite possible that the surface as at present defined $CW^{\frac{2}{3}}$ does not give the very best agreement in comparisons of different individuals. The main point is that metabolism in warm-blooded animals is not proportional to the weight W but to W^n where n is certainly not far from 2/3.

On the whole, looking at the problem from a broad point of view, it seems pretty certain that the surface law of Rubner is generally proved as far as the metabolism of warm-blooded animals are concerned.

In the following pages, I shall try to find out a physical significance of Rubner's generalization and other facts regarding the influence of temperature on metabolism in both warm and cold blooded animals. We can look at the problem of metabolism of different warm-blooded animals from the following considerations:—

(1) The body temperature of warm-blooded animals is normally much higher than the surrounding air. In the case of some birds, sparrow, hen, etc., the body temperature is about 42°. In the case of rabbit it is 39°.6 and in the case of dog it is 39°.2.

(2) Experimental results have shown that radiation is the most important factor in the loss of heat from animal body.. Let us assume that a metallic ball of radius r and density of the material ρ, is placed in air at say T_0 and we are supplying heat to the ball so that the temperature of the ball may be kept constant at T where T is greater than T_0. Now in order to maintain this constant temperature a supply of heat has to be given to the ball, otherwise the body loses heat and cools down to the temperature of the surrounding air (T_0). From Stefan's law of radiation, we know that the loss of energy from the surface is equal to $4\pi\gamma^2\sigma(T^4 - T_0)$, where $4\pi\gamma^2$ is the surface of the body in question and σ is Stefan's constant. Therefore the rate of supply of heat to the body per unit mass in order to keep the body temperature constant to T is equal to

$$\frac{4\pi\gamma^2\sigma\ (T^4 - T_0^4)}{4/3\pi\gamma^3\rho} = \frac{3\rho\sigma}{\gamma}(T^4 - T_0^4)$$

From the foregoing relation it will be seen that the rate of supply of heat per unit mass varies inversely as the radius of the body in question. In other words, a small ball of the same material requires a much larger quantity of heat per unit mass of the body. Let us apply these considerations to the question of metabolism in animals. Ordinarily warm-blooded animals are surrounded by air of a much lower temperature than the temperature of the animal body. In other words, the animal is constantly giving out heat to the outside surroundings mainly by radiation and in order that this phenomenon can take place the metabolism of the system should increase in order to keep the body temperature constant. From the foregoing considerations it will be evident that the amount of heat per unit weight of the body lost by the animal due to this radiation is greater, the smaller the size of the animal. This conclusion is actually corroborated by experiments. Consequently from physical principles it follows that the loss of heat per unit weight of the body and the consequent metabolism in the animal body to keep up this loss of heat is greater the smaller the size of the animal.

From the relation already obtained it is seen that the rate of supply of heat per unit mass is proportional to the difference in temperature between the body and the surrounding air; in other words, the greater is the difference in temperature the greater is the rate of supply of energy per unit mass of the substance. Consequently when a warm-blooded animal is surrounded by air which is colder than the air with which it is normally surrounded, his rate of supply of energy and consequently his metabolism should also increase and that is the reason why the metabolism in the case of warm-blooded animals increases with the fall of surrounding temperature.

We have already shown that the loss of energy from the surface $= 4\pi\gamma^2\sigma (T^4 - T_0^4)$. Now if we express this loss per unit surface, the expression becomes $\sigma(T^4 - T_0^4)$; in other words, the question of radius or the size of the body does not come into consideration and the loss of energy per unit surface becomes proportional only to the difference between the body temperature and that of the surrounding air. This has been experimentally obtained by Rubner who has obtained the following results with guinea pig:

Temperature	CO_2
0°	2.91
11°	2.15
21°	1.77

If we calculate the metabolism according to the relation $\sigma(T^4 - T_0^4)$, we find that the ratio of the metabolisms at 0° and 11° is about 1.2, whilst the observed ratio of the metabolism is about 1.3; the calculated value between 21° and 26° is 1.38 and the observed value is 1.2, taking the average temperature of guinea pig to be 38.2. Hence we get a physical significance of Rubners law.

From the foregoing pages, it will be evident that Rubner's generalization would be applicable mainly to warm-blooded animals, because usually they maintain a higher body temperature irrespective of the temperatures of the surroundings and the laws of radiation would be applicable to such cases.

In the case of cold-blooded animals the body temperature is only slightly higher than the temperature of the surroundings and the foregoing considerations are not applicable in these cases and Rubner's generalization is not valid for cold-blooded animals.

We have already suggested that life principle depends essentially on the activity of the catalyst or the enzymes existing in the body. In the foregoing pages, we have observed that usually smaller animals have more metabolism per unit weight of the body than larger animals; in other words weight for weight, the catalysts or the enzymes in smaller animals are more reactive than the catalysts in larger animals. It sounds very queer that the activity of the enzymes present in the system of a dog is much greater than the activity of those present in the case of a man or we have to assume that the amount of the catalyst per unit weight of the body is much greater in the case of smaller animals than in large animals. It will be seen in the subsequent discussion that the former proposition is more reasonable than the latter. In other words, we are led to the conclusion that the physical activity and the amount of oxidation per unit weight of the body are much greater in the case of a dog than in the case of a man. Even a most casual observation of the domesticated animals has shown that as a rule, small animals do not live so long as large ones. As a general rule, it may be said that a large animal takes more time than a small one to reach maturity and it has been inferred from this that the length of the period of growth is in proportion to longevity. Hence small animals with intensive metabolism live a relatively short time. Large animals with more sluggish metabolism live a longer time. We have already mentioned that Rubner's view is that a definite sum of living action or energy transformation determines the physiological end of life.

There are chemical analogies to these biological facts. Sabatier and his colleagues have shown that when metallic nickel, which is used as a catalyst in the hydrogenation processes, is prepared under suitable conditions at as low a temperature as possible, the activity of the catalyst is extremely great but it loses its activity very readily. From our experience with other catalysts, we know that an extremely active catalytic surface deteriorates also very rapidly. In other words, an extremely active catalytic surface is more liable to be poisoned or undergo other changes which would effect its activity as a catalyst than the surface of moderately active catalysts.

Consequently it seems probable that in the biological processes of metabolism extremely active catalysts are likely to lose their activity more readily than moderately active catalysts. In other words, the catalysts which accelerate the metabolism or oxidation in the case of dogs induces in an unit time more oxidation than the moderately active catalysts present in the human system, but the more active catalyst present in smaller animals is more liable to lose their activities by poisoning or other alterations than the moderately active catalysts present in the human body and that is why death is more rapid in the case of animals having more active catalysts than in animals having moderately active ones. In this connection the following experiments of Slonaker[1] on rats will be of interest. Slonaker kept four albino rats in cages like the old-fashioned revolving squirrel cages, with a properly calibrated odometer attached to the axle, so that the total amount of running which they did in their whole lives could be recorded.

---

[1] J. Animal Behavior, 2, 20 (1912).

It was observed that the amount of exercise taken by these rats was astonishingly large. For a rat to run 5,447 miles in the course of its life is indeed a remarkable performance. Now these four rats attained an average age at death of 29.5 months. But three control rats confined in stationary cages so that they could only move about to a limited degree, but otherwise under conditions, including temperature, identical with those in the revolving cages, attained an average age at death of 40.3 months. All were stated to have died of "old age". From this experiment it clearly appears that the greater the total work done, or total energy output, the shorter the duration of life, and vice versa.

We shall now try to explain the possibility of acclimatization of warm-blooded animals from this point of view. As we have already mentioned, when there is a fall in the surrounding temperature the metabolism of warm-blooded animals is increased; in other words when a warm-blooded animal is brought from a warmer climate to a cooler climate its metabolism and the catalytic activity of the body enzymes are increased. In other words, there is a strain in the system. In the case of human beings this relation should also be valid. We have already mentioned that usually 20% of the body surface is exposed to air in the case of human beings, the remaining 80% is covered by clothes, so that we have to consider only the exposed portion. Now even for this comparatively small exposed portion the metabolism of the body should increase on lowering the temperature of the surroundings. Consequently the catalyst in the body would be activated; but, as Rubner has shown, the standard metabolism cannot undergo rapid changes as the oxidative energy of the cells is adapted to the usual conditions regarding the loss of heat and is altered very gradually with those conditions; hence the system of a human being or an animal brought from a warmer climate to a cooler climate will be in a state of strain.

In the case of cold-blooded animals it is evident that the metabolism is much slower than in the case of warm-blooded animals. Hence the catalytic activity of the enzymes present in cold-blooded animals is not as great as those in the warm-blooded animals of the same size. Consequently the duration of life of a cold-blooded animal is usually greater than that of a warm-blooded animal of the same size and this is corroborated by evidence from biology, because experience show that cold-blooded animals live much longer than warm-blooded animals of the same size.

When warm-blooded animals are transported from a warmer climate to a cooler climate, metabolism is increased. The effect of this is that the catalytic activity of the enzymes has to increase in order to produce greater combustion in a unit of time.

I have already emphasised that when the catalyst is made to work at a greater speed than the normal one the life period of the catalyst is decreased.

Consequently one effect of the transportation of a warm-blooded animal from a warmer climate to a cooler climate will be to activate the enzymes in the body and it will lead to its shortening of the life period.

The temperature of a warm-blooded animal remains constant whatever may be the temperature of the surroundings. Consequently the catalyst has to work at the same temperature irrespective of the temperature of the outside surroundings. Thus, in the case of warm-blooded animals, the question of ageing of the catalyst at a greater rate due to the increase in temperature does not arise, because the catalyst works at a constant temperature which is the body temperature of the animal in question provided the external temperature is less than the body temperature. So the main effect of transporting a warm-blooded animal from a warmer country to a colder country is to increase the activity of the body enzymes and to increase the metabolism and to shorten the life period of the animal in question. Now if the enzymes which were used to generate smaller quantity of heat in a warmer climate are required to produce greater quantity of heat in a cooler climate, they will, by and by, be tired out. In course of time the individual or the animal in question would feel the strain and it seems possible that as years go he will feel the strain more and more. It seems probable thus that an human being transported from a warmer climate to a cooler climate will feel the cold more and more as years go by.

On the other hand, if a warm-blooded animal is transported from a cooler climate to a warmer climate, let us see what will be the result on his system by this transportation. As soon as he is surrounded by a warmer atmosphere the amount of metabolism which he was used to produce in a cooler surrounding has to become less because now he is surrounded by a warmer atmosphere. Consequently the catalyst inside the body has to work less in a warmer climate than in a colder climate. Hence the life period of the individual in question is likely to be increased when he is transported from a cooler to a warmer climate provided that the exterior temperature is not greater than his body temperature.

I am of the opinion, therefore, that it is more advantageous for a man living in a colder climate to come to a warmer climate than the reverse. When a warm-blooded animal has to live in a country where the outside temperature is usually greater than the body temperature, then the animal will age and grow old and die more readily than an animal living in a cold country; because at the higher temperature, the body catalysts will age more quickly. Thus this case of an warm-blooded animal will be allied to that of a cold-blooded animal.

In this discussion, I have all along neglected the consideration of humidity and its influence on human beings and animals.

There is another factor that of the color of the skin surface; animals with deeper color are likely to radiate heat more readily than animals with fair complexion.

I have emphasised that the metabolism of cold-blooded animals is much less than in the case of warm-blooded animals under the same conditions; in other words, the enzymes present in cold-blooded animals are not as active as those present in warm-blooded animals. We have also observed that the body temperature of a cold-blooded animal is usually slightly higher than the temperature of the surrounding air and that the metabolism in the case of a cold-blooded animal goes on increasing as the surrounding temperature is increased.

Let us see what takes place when a cold-blooded animal living in a warmer country is taken to a cooler country. The metabolism in the system will decrease and the animal has to live a life of lesser intensity and possibly with a lesser sense and feeling of well being. The enzymes have to generate lesser quantities of heat in the cool atmosphere and consequently their period of life will be increased and the animal is expected to live a longer life in a cooler surrounding. Moreover, the body catalysts will not age as rapidly in the cooler surroundings as would have been the case in a warmer country. Consequently these two factors will both lead to a greater longevity of the cold-blooded animal in question when transported from a warmer to a cooler country.

On the other hand, when a cold-blooded animal habituated to a cooler locality, is transported to a warmer country, his metabolism in an unit of time will be increased and the catalysts in the body have to perform more work. Consequently the period of activity of the catalyst will be decreased and the life of the animal is likely to be shortened, though the animal has a more intense and active life in a warm surrounding. Moreover, in a warmer country the body catalyst is likely to age more rapidly than in a cool country. Consequently the effect of both these factors is that old age and death would follow more rapidly in a cold blooded animal transported from a cooler atmosphere to a warmer place.

Summary and Conclusion

1. (a) Rubner from his experiments concluded that metabolism in different warm-blooded animals was constant when expressed per square metre of the body surface. (b) Experimental results show that smaller animals have greater metabolism in a unit time per kilogram than larger animals. (c) The metabolism of warm-blooded animals increases when there is a fall in the temperature of the surroundings. These biological facts have been explained from Stefan's law of radiation.

2. The physical activity and amount of oxidation per unit weight of the body are greater in the smaller animals than in the larger ones. In the process of metabolism, extremely active catalysts are likely to lose their catalytic activity more readily than moderately active catalysts and that is why death is more rapid with smaller animals than with larger ones.

3. The effect of transporting a warm-blooded animal from a warmer country to a colder country is to increase the activity of the body enzymes and to increase the metabolism and to shorten the life of the animal in question.

If a warm-blooded animal is transported from a cooler climate to a warmer climate, the catalytic activity of the enzymes and the metabolism are decreased. Hence the longevity of the animal in question is likely to be increased.

When the warm-blooded animal has to live in a country where the outside temperature is usually greater than the body temperature, then the animal is likely to age and grow old and die more readily than an animal living in a cold country.

4. When a cold-blooded animal is transported from a warmer to a cooler country, the metabolism is decreased and the body enzymes will not age as rapidly as they would do in a warmer country. Consequently both these factors lead to a greater longevity of the cold-blooded animal by this transportation.

When a cold-blooded animal is taken from a cooler to a warmer country, the metabolism will be increased and the enzymes will age more rapidly. Hence, the effect of both these factors will be that old age and death will follow more readily, though the animal will live a more intense in a warmer country.

Chemical Laboratory,
Allahabad University,
Allahabad, India.

THE REDUCTION OF NITROUS OXIDE*

BY M. L. NICHOLS AND I. A. DERBIGNY

This study was made as part of the investigation to determine the mechanism of the reduction of nitric acid, since nitrous oxide is a secondary product[1] of this reduction. The nitrous oxide was reduced by bubbling it through aqueous solutions of the different reducing agents, which were placed in E, Fig. 1.

The reduction with hydrogen by slow combustion at a red hot platinum surface has been used as a method for the quantitative determination of nitrous oxide. Winkler[2] obtained nitrogen and water by this method but Kemp[3], using the same method, found that ammonia was also formed. Lunge[4] obtained quantitative reduction to nitrogen and water by low temperature combustion with hydrogen at a platinum surface. Pascal[5] states that nitrous oxide is reduced to nitrogen by sulfur dioxide, if the temperature and sulfur dioxide concentration are high. At this laboratory, Coblens and Bernstein[6] obtained almost complete reduction to ammonia by shaking the nitrous oxide with a solution of titanous chloride.

Experimental

The nitrous oxide was prepared by the method of Victor Meyer[7] from pure sodium nitrite and hydroxylamine sulphate and collected in a gasometer over water which had been saturated previously with pure nitrous oxide. Its purity was determined by slow combustion with hydrogen in a Hempel combustion pipette L (Fig. 1) as described by Milligan. Six analyses starting with about 18 cc. of nitrous oxide gave a mean purity of 99.8%, with an average deviation from the mean of 0.2%.

Analytical Methods

The ammonium salts were determined by Milligan's modification of Suler's[8] method. The method used for the determination of hydroxylamine in the presence of ammonium salts was reduction with a titanous salt solution as recommended by Milligan. Six analyses taking 0.026 – 0.077 g. of ammonia in the presence of 0.05 – 0.25 g. of hydroxylamine gave results on the average too small by 0.25 milligrams ± 0.06 milligrams corresponding to a relative error of – 0.7% ± 0.4%.

---

* Contribution from the Baker Laboratory of Chemistry at Cornell University.

[1] Armstrong: J. Chem. Soc., **32**, 56 (1877); Bancroft: J. Phys. Chem., **28**, 493 (1924); Dhar: J. Phys. Chem., **29**, 152 (1925).

[2] Winkler: "Lehrbuch tech. Gasanalyse," 3rd Ed., 190 (1901).

[3] Kemp: Chem. News, **71**, 108 (1895).

[4] Lunge: Ber. **14**, 2190 (1881).

[5] Pascal: "Synthesis and Industrial Catalysis," 348 (1925).

[6] Coblens and Bernstein: J. Phys. Chem., **29**, 750 (1925).

[7] Meyer: Ann., **175**, 141 (1875); Milligan: J. Phys. Chem., **28**, 544 (1924).

[8] Suler: Z. Elektrochem., **7**, 839 (1901).

Six analyses taking 0.1 – 0.2 g. of ammonia and 0.1 – 0.2 g. of hydroxylamine in the presence of large amounts of stannous chloride gave results for ammonia on the average too small by 0.3 milligram ± 0.1 milligram, corresponding to a relative error of 0.2% ± 0.1%. The results for hydroxylamine showed an average error of 0.2 milligrams ± 0.2 milligrams, corresponding to a relative error of 0.1% ± 0.1%.

The strength of the solution of titanous chloride was determined by precipitation with ammonium hydroxide and bromine water and ignition to titanic oxide[1]. The solution was found to contain 20.6 per cent $TiCl_3$. All of the solutions of titanous chloride used in the subsequent experiments were prepared by diluting this solution with the proper amount of water.

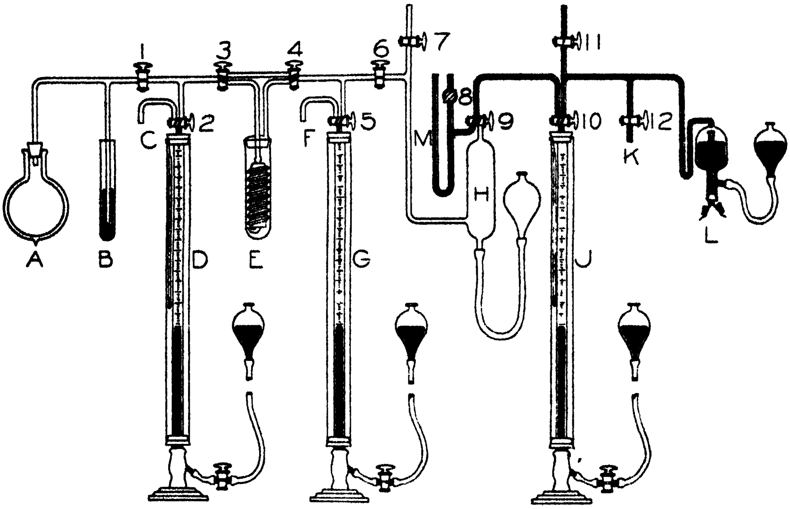


Fig. 1

The solution of stannous chloride was prepared by boiling a large excess of pure tin with concentrated HCl until hydrogen was no longer liberated, adding small amounts of water from time to time to replace that lost by boiling. After filtration the solution was kept in a stoppered bottle in contact with pure tin. The strength of the solution was determined by adding an excess of iodine and titrating the excess with sodium thiosulphate[2]. The solution was found to contain 0.3705 grams of $SnCl_2$ per cc. In preparing the solutions for use in the experiments, a slight excess over the theoretical amount of this approximately standard solution[3] was diluted with the proper amount of water and the resulting solution standardized with iodine as before.

---

[1] Treadwell and Hall: Vol. II, 100 (1911).

[2] Hallett: J. Soc. Chem. Ind., **35**, 1087 (1916).

[3] It was impossible to keep the stannous chloride solution without some oxidation of the stannous chloride to stannic chloride.

Apparatus and Manipulation

The apparatus used in these experiments is shown in Fig. 1. Carbon dioxide snow[1] was placed in the liter unsilvered Dewar flask, A, surrounded by a cotton jacket to control the rate of evaporation of the snow. The pressure on the system was regulated by means of the large test tube, B, containing mercury. The reducing agents were placed in E which is a modification[2] of a Friedrichs[3] spiral wash bottle. The tubes C, F, and K served as a means of introducing gases into the apparatus and as a channel through which the burettes were cleaned. All of the burettes used were calibrated at 20°C. Atmospheric pressures were determined by means of a standard, high-grade barometer fitted with a vernier. The large tube H was filled with concentrated sodium hydroxide solution. The CO_2 used to wash out the gases was absorbed by the NaOH in this tube. The final combustion was made in the Hempel pipette L and the hydrogen introduced through K. The manometer M was used as an indicator for bringing the gas in the burette J to exactly atmospheric pressure.

About 100 grams of carbon dioxide snow was placed in the flask A and the carbon dioxide allowed to pass into the bottle E and through the by-pass between stopcocks 3 and 4 and out through stopcock 7. The apparatus was washed out in this manner until the gas bubbling into H when stopcock 7 was closed, was completely absorbed by the sodium hydroxide solution. This showed that all of the air had been washed out of the solution in E as well as out of the entire apparatus. To accomplish this required usually from forty to eighty minutes.

To test the accuracy of the apparatus the bottle E was filled with distilled water and the apparatus washed free from air as previously described. Nitrous oxide was introduced into the burette D and measured at 20°C. and atmospheric pressure. The gas was then passed back and forth between D and G through E and returning through the by-pass between stopcocks 3 and 4. The gas was then finally passed into H and the carbon dioxide from the flask allowed to flow through E by opening stopcock 1. During the passing of the nitrous oxide back and forth through E stopcocks 1, 6 and 7 were closed and the tube connecting 6 and 7 with H was filled completely with the solution of sodium hydroxide by raising the level-bulb attached to H. The carbon dioxide was able to wash out all of the nitrous oxide from the water and the sodium hydroxide solution, since nitrous oxide does not form a stable compound[4] with either. The time required to wash out all traces of the gas was between 15 and 20 minutes. After all of the carbon dioxide had been absorbed by the sodium hydroxide, the gases remaining in the top of H were drawn into the burette J, the tube between stopcocks 9 and 10 having been previously filled completely with mercury. The mercury in the pipette L was forced to the entrance of the tube K into the horizontal tube, and the volume of the horizontal tube between the entrance of K into this tube and the tube joining stopcocks 10 and 11 was determined and a correction applied. The hydrogen, having been purified and measured at 20°C. and atmospheric pressure, was passed into L. The spiral was then heated and the gas from H, having been likewise measured in burette J was passed into the pipette and determined as previously described.

---

[1] Milligan: J. Phys. Chem., **28**, 544 (1924).

[2] Milligan: Ind. Eng. Chem., **16**, 889 (1924).

[3] Friedrichs: Z. anal. Chem., **50**, 175 (1911).

[4] Milligan: J. Phys. Chem., **28**, 544 (1924).

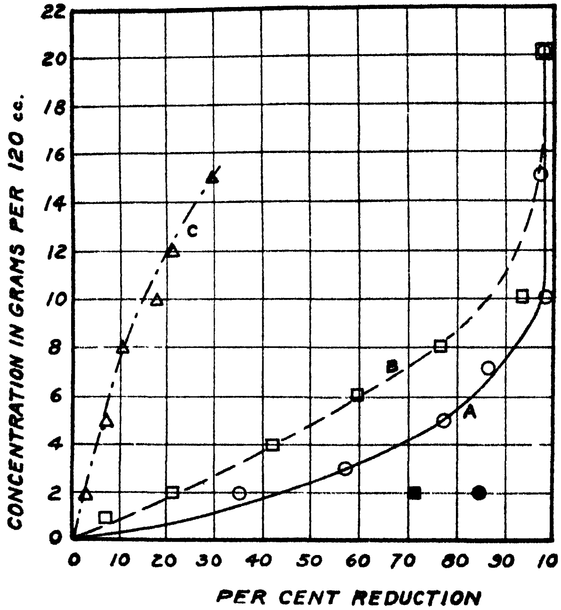


FIG. 2
The Reduction of Nitrous Oxide:
Variation of the Concentration of Reducing Agent at Constant Temperature
Curve A = Titanous Chloride
Curve B = Stannous Chloride
Curve C = Sodium Sulfite
Note—Solid black points are for a longer time of contact.

Four determinations taking about 20 cc. of nitrous oxide gave theoretically correct results while two determinations on 18 and 30 cc. of nitrous oxide gave results too small by 0.2 cc., corresponding to relative errors of 1.1% and 0.65%.

The Reduction of Nitrous Oxide by Titanous Chloride

The nitrous oxide was passed through solutions of titanous chloride and the residual gas analyzed by combustion, as previously described. The temperature was kept constant by almost completely immersing the wash bottle E in a water bath. A large beaker fitted with a siphon arrangement and inlet tube was found to serve the purpose adequately. The temperature was measured by means of a thermometer which had been calibrated against a standard thermometer certified by the Bureau of Standards. After passing the gas through E a definite number of times (see table) and washing the residual gas into H with carbon dioxide, the solution in E was divided into two parts and analyzed for ammonia and hydroxylamine. The result of these determinations are shown in Table I and Fig. 2, Curve A. All of the measurements were made at 20°C. and atmospheric pressure. Experiment No. 8 shows the results of increasing the time of contact. In this, and all the other groups of experiments using titanous chloride as the reducing agent, the only product found was ammonia. Any nitrogen formed would have been definitely indicated by the combustion data on the residual gas. If hydroxylamine were formed it would have been detected in the analysis of the solution. On examining Table I it can be seen that the amount of ammonia found was sufficiently near the theoretical amount to warrant the conclusion that no other products were formed, or if other products were formed, they were not the final products of the reduction. The fact that the difference between the theoretical amount and the experimental amount is nearly constant further warrants this view, since it is not likely that the amount of a substance formed would remain constant under such varying conditions.

TABLE I

The Reduction of Nitrous Oxide with Titanous Chloride:
Variation of the Concentration of Titanous Chloride.

Temperature 20°C.
Volume of HCl (Sp. Gr. 1.17)—0.5 cc.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 8 where was 45.
Time of contact—120 min. in all except No. 8 where was 540 min.

Expt. No.	$TiCl_3$ G	N_2O taken Mg.	N_2O reduced Mg.	NH_3 calc. Mg.	NH_3 found Mg.	Per cent reduction
1	2	34.7	12.0	9.3	9.0	34.7
2	3	35.7	20.2	15.6	15.1	56.4
3	5	35.4	27.2	21.1	20.8	77.0
4	7	36.1	30.7	23.8	23.4	85.2
5	10	35.7	35.0	27.1	26.6	98.0
6	15	36.4	35.4	27.4	27.0	97.1
7	20	36.1	35.4	27.4	27.3	98.0
8	2	35.5	29.8	23.1	22.9	84.0

From the preceding group of experiments it can be readily seen that 10 grams of titanous chloride in 120 cc. of solution is the most favorable concentration and was used for the next series of experiments to establish the effect of varying the temperature. These determinations were carried out as before, all of the other factors except the temperature being kept constant. The results are shown in Table II and Fig. 3, Curve A. Experiment No. 9 shows the effect of increasing the time of contact.

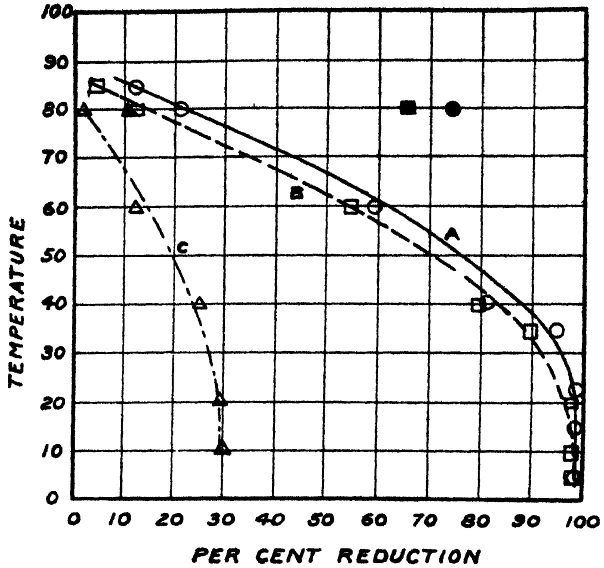


Fig. 3

The Reduction of Nitrous Oxide:
Variation of the Temperature with Constant Concentration of Reducing Agent.
Curve A = Titanous Chloride
Curve B = Stannous Chloride
Curve C = Sodium Sulfite
Note—Solid black points are for a longer time of contact.

Table II

The Reduction of Nitrous Oxide with Titanous Chloride: Variation of the Temperature.

Amount of $TiCl_3$—10 gr.
Volume of HCl (Sp. Gr. 1.17)—0.5 cc.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 9 where was 45.
Time of contact—120 min. in all except No. 9 where was 540 min.

Expt. No.	Temp. °C.	N_2O taken Mg.	N_2O reduced Mg.	NH_3 calc. Mg.	NH_3 found Mg.	Per cent reduction
1	5	35.9	35.2	27.3	27.2	98.0
2	15	35.9	35.2	27.3	27.3	98.0
3	23	35.6	34.9	27.0	27.0	98.0
4	35	35.9	33.8	26.2	25.8	94.1
5	41	35.9	29.2	22.6	22.3	81.2
6	60	35.2	20.8	16.1	16.1	59.0
7	80	35.9	7.8	6.0	5.7	21.6
8	85	34.5	4.2	3.3	2.8	12.2
9	80	35.8	26.2	20.3	20.0	73.3

Using the same concentration of titanous chloride, as in the previous group, and a temperature of 20°C., the acid concentration was varied. Concentrated hydrochloric acid, specific gravity 1.17, was used. The results obtained are shown in Table III and Fig. 4, Curve A. In experiment No. 8, an amount of sulphuric acid equivalent to 25 cc. of hydrochloric acid was used. In experiment No. 9, 25 cc. of hydrochloric acid was added and then neutralized with an equivalent amount of sodium hydroxide. In experiment No. 10, a piece of platinized platinum foil was used as a catalyst. The foil was placed at the mouth of the entrance tube into E.

TABLE III

The Reduction of Nitrous Oxide with Titanous Chloride: Variation of the Acidity.

Amount of $TiCl_3$—10 gr.
Temperature—20°C.
Volume of solution—120 cc.
Number of passages of gas—10.
Time of contact—120 min.

Expt. No.	Vol. HCl Sp. gr. 1.17 Cc.	N_2O taken Mg.	N_2O reduced Mg.	NH_3 calc. Mg.	NH_3 found Mg.	Per cent reduction
1	2	36.3	35.3	27.3	27.0	97.1
2	5	35.6	33.5	25.9	25.6	94.0
3	10	35.3	28.5	22.1	22.1	80.8
4	15	36.0	25.3	19.6	18.9	70.3
5	25	35.5	7.0	5.5	5.1	19.8
6	35	35.8	0.0	0.0	0.0	0.0
7	50	35.5	0.0	0.0	0.0	0.0
8	(1)	35.5	7.8	6.0	5.7	22.0
9	(2)	36.2	19.2	14.8	14.8	52.9
10	25(3)	35.3	11.3	8.7	8.4	32.0

1—7.48 cc. H_2SO_4 the equivalent of 25 cc. HCl used.
2—25 cc. HCl neutralized with NaOH.
3—Platinized platinum used as catalyst.

The Reduction of Nitrous Oxide by Stannous Chloride

In all of the experiments using stannous chloride, hydroxylamine was the only product formed. The results of varying the concentration of stannous chloride at constant temperature and time of contact are shown in Table IV and Fig. 2, Curve B. Experiment No. 8 shows the effect of increasing the time of contact.

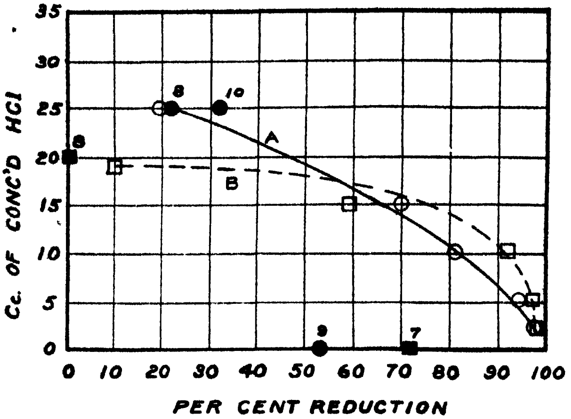


Fig. 4

The Reduction of Nitrous Oxide:
Variation of the Acid Concentration at Constant Temperature and Reducing Agent Concentration.

Curve A = Titanous Chloride
Curve B = Stannous Chloride

Note—For the conditions of the experiments shown by the solid black points see the corresponding experiment in Tables III and VI.

Table IV

The Reduction of Nitrous Oxide with Stannous Chloride: Variation of the Concentration of Stannous Chloride.

Temperature—20°C.

Volume of solution—120 cc.

Number of passages of gas—10 in all except No. 8 where was 45.

Time of contact—120 min. in all except No. 8 where was 540 min.

Expt. No.	$SnCl_2$ G.	N_2O taken Mg.	N_2O reduced Mg.	NH_2OH calc. Mg.	NH_2OH found Mg.	Per cent reduction
1	20	35.8	35.1	52.6	53.3	98.0
2	10	35.4	32.9	49.5	50.0	93.0
3	8	36.1	27.6	41.5	41.6	76.5
4	6	35.6	21.2	31.8	32.1	59.4
5	4	35.3	14.8	22.2	22.2	42.0
6	2	35.5	7.4	11.1	10.8	20.8
7	1	35.9	2.5	3.7	3.4	6.9
8	2	35.5	25.1	38.0	38.5	71.3

The temperature was then varied, Table V and Fig. 3, Curve B. The effect of increased time of contact is shown in experiment No. 9.

Table V

The Reduction of Nitrous Oxide with Stannous Chloride: Variation of the Temperature.

Amount of $SnCl_2$—20 gr.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 9 where was 45.
Time of contact—120 min. in all except No. 9 where was 540 min.

Expt. No.	Temp. °C.	N_2O taken Mg.	N_2O reduced Mg.	NH_2OH calc. Mg.	NH_2OH found Mg.	Per cent reduction
1	5	36.3	35.6	53.4	53.8	98.0
2	10	35.6	34.9	52.3	52.7	98.0
3	20	35.9	34.9	52.3	52.4	97.0
4	35	35.7	32.2	48.3	49.0	90.1
5	40	35.4	28.7	43.0	43.2	81.0
6	60	35.4	19.5	29.2	29.1	55.0
7	80	35.6	4.6	6.9	6.4	12 9
8	85	35.3	1.8	2.7	2.3	5.0
9	80	35.3	23.3	34.9	35.1	66.0

In Table VI and Fig. 4, Curve B, is shown the effect of varying the acid concentration at constant temperature and concentration of reducing agent. In experiment No. 7, 20 cc. of hydrochloric acid was neutralized with sodium hydroxide. Experiment No. 8 shows the effect of adding a quantity of sulphuric acid equivalent to 20 cc. of hydrochloric acid.

Table VI

The Reduction of Nitrous Oxide with Stannous Chloride: Variation of the Acidity.

Amount of $SnCl_2$—20 gr.
Temperature—20°C.
Volume of solution—120 cc.
Number of passages of gas—10
Time of contact—120 min.

Expt. No.	Vol. HCl Sp. gr. 1.17 Cc.	N_2O taken Mg.	N_2O reduced Mg.	NH_2OH calc. Mg.	NH_2OH found Mg.	Per cent reduction
1	2	35.9	35.2	52.8	53.1	98.0
2	5	35.5	34.5	51.7	52.2	97.0
3	10	36.2	33.4	50.1	50.3	92.2
4	15	35.1	20.7	31.1	31.5	59.0
5	18	35.6	3.5	5.3	5.0	9.9
6	20	35.6	0.0	0 0	0.0	0.0
7	(1)	35.3	25.1	37.6	37.8	71.0
8	(2)	36.5	0.0	0.0	0.0	0.0

1—20 cc. HCl neutralized with NaOH.
2—6 cc. H_2SO_4 the equivalent of 20 cc. HCl used.

The Reduction of Nitrous Oxide by Sulphurous Acid

A solution of sulphurous acid containing 0.0431 grams per cc. was used and 29 per cent reduction to nitrogen was obtained. No further experiments were performed with sulphurous acid due to the fact that the carbon dioxide and nitrous oxide drive the sulphur dioxide from solution and thereby change the concentration. Sodium sulphite was used instead of sulphurous acid.

The Reduction of Nitrous Oxide by Sodium Sulphite

Sodium sulphite reduces nitrous oxide to nitrogen. The results of varying the concentration of sodium sulphite are shown in Table VII, and Fig. 2, Curve C. Experiment No. 7 shows the result of increased time of contact upon the reduction. Using a concentration of 15 grams of sodium sulphite in 120 cc. of solution, the effect of temperature was studied Table VIII, Fig. 3, Curve C. The effect of increased time of contact is shown in experiment No. 6. No acid was used in these experiments as sulphur dioxide is formed with a corresponding decrease in the concentration of the sodium sulphite.

TABLE VII

The Reduction of Nitrous Oxide with Sodium Sulphite:
Variation of the Concentration of Sodium Sulphite.

Temperature 20°C.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 7 where was 45.
Time of contact—120 min. in all except No. 7 where was 540 min.

Expt. No.	Na_2SO_3 G.	N_2O taken Mg.	N_2O reduced Mg.	N_2 calc. Mg.	N_2 found Mg.	Per cent reduction
1	2	35.5	1.1	0.7	0.7	3.0
2	5	35.5	2.4	1.6	1.6	6.9
3	8	35.6	3.9	2.5	2.5	10.9
4	10	35.8	6.4	4.0	4.0	17.8
5	12	36.2	7.8	4.9	4.9	21.6
6	15	35.4	10.6	6.7	6.7	30.0
7	15	35.7	30.0	18.9	18.9	84.0

E. M. F. and Conductance Measurements

For reasons which are given in the theoretical division of this paper, it was found necessary to make a series of e.m.f. determinations upon the solutions of the reducing agents used, and upon a saturated solution (20°C.) of nitrous oxide, containing varying amounts of hydrochloric acid. These determinations were made by means of a calomel electrode against a platinum electrode in the case of the solutions of the metallic salts, and against an electrode of platinum black in the nitrous oxide experiments. A Leeds and Northrup

TABLE VIII

The Reduction of Nitrous Oxide with Sodium Sulphite: Variation of the Temperature.

Amount of Na_2SO_3—15 g.
Volume of solution—120 cc.
Number of passages of gas—10 in all except No. 6 where was 45.
Time of contact—120 min. in all except No. 6 where was 540 min.

Expt. No.	Temp. °C	N_2O taken Mg.	N_2O reduced Mg.	N_2 calc. Mg.	N_2 found Mg.	Per cent reduction
1	10	36.4	10.6	6.7	6.7	29.1
2	20	37.0	11.0	7.0	7.0	29.8
3	40	35.5	8.9	5.8	5.6	25.0
4	60	35.6	4.2	2.7	2.7	11.9
5	80	35.8	0.7	0.67	0.45	2.0
6	80	35.5	3.9	2.5	2.5	11.0

TABLE IX

Voltage Measurements of Solutions of Titanous Chloride, Stannous Chloride, Sodium Sulphite and Nitrous Oxide, in Solutions containing varying Amounts of Hydrochloric Acid.

Cc. HCl	Volts	Corrected reading[1]
	Titanous Chloride 10 grams, in 120 cc. of solution	
2	0.270	+0.023
10	0.230	−0.018
15	0.207	−0.041
20	0.189	−0.059
	Stannous Chloride 20 grams, in 120 cc. of solution	
2	0.057	−0.191
10	0.081	−0.167
15	0.112	−0.138
20	0.119	−0.129
	Sodium Sulphite 12 grams, in 120 cc. of solution	
0	0.035	−0.213
	Nitrous Oxide Saturated solution at 20°C. 120 cc. solution	
0	0.599	+0.847
2	0.603	+0.851
10	0.611	+0.859
15	0.625	+0.873
20	0.641	+0.889

---

[1] By subtracting 0.2475, the value of the calomel electrode.

Type K potentiometer was used in making the measurements. Results are given in Table IX. The values obtained are in agreement with those of B. Neumann[1]. In order to refer the values to a normal hydrogen electrode, it was necessary to add the value of the calomel electrode to the voltages obtained with the solutions of nitrous oxide since the calomel electrode is negative with respect to platinum black in this solution. The solution was kept saturated with nitrous oxide by bubbling the gas through the solution during the experiment.

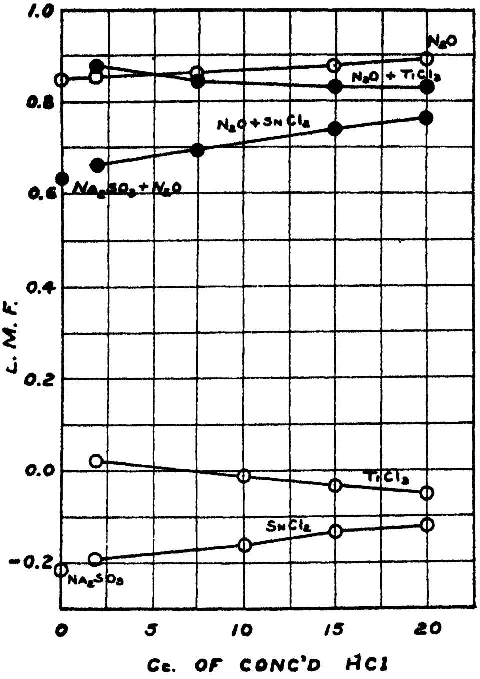


FIG. 5
E. M. F. Measurements
Note—Solid black points are derived by taking the algebraic sum of the experimentally determined values.

In order to determine the change in conductivity of distilled water when saturated with nitrous oxide, 100 cc. of distilled water was placed in a large test tube and the conductivity measured. Table X, experiment No. 1. The water was then saturated with pure nitrous oxide by bubbling the gas through the solution and the conductivity again measured. Table X, experiment No. 2. C is the conductivity in reciprocal ohms of the solution between the electrodes. Leeds and Northrup apparatus was used throughout. The specific conductivity of the distilled water used was about 2.0×10^{-6}. The results obtained showing an increase in conductivity would indicate that $(NOH)_2$ was formed (See discussion).

---

[1] Neumann: Z. physik. Chem., 14, 193 (1894).

TABLE X

Conductivity Measurements

Expt. No.	Temp. °C.	C	ΔC
1	25.22	1.6×10^{-5}	— — —
2	25.18	2.1×10^{-5}	5×10^{-6}

Discussion

From the preceding experimental work it has been shown that, with all of the reducing agents used, the percentage reduction for a definite time of contact, (1) increases with an increase in concentration of the reducing agent, (2) decreases with a rise in temperature and, (3) in the case of titanous chloride and of stannous chloride, decreases with increased acid concentration. The experimental work also shows that the only effect of these variables is to change the percentage reduction and never the nature of the final reduction product with a given reducing agent.

It would be natural to expect in the reduction of a gas by liquid reagents that no reduction would take place, except with gas which dissolves in the liquid. In the reduction with stannous chloride the only product obtained is hydroxylamine, which can only be explained on the assumption that hydration of nitrous oxide occurs, which we believe takes place with the formation of hyponitrous acid.

$$N_2O + H_2O = (NOH)_2$$

On this basis it is possible to explain all of the results obtained. A direct reduction of nitrous oxide without the addition of water would give an unsymmetrical product and only a fifty percent yield of hydroxylamine.

Since in every case with a given reducing agent the final product is always the same, the reducing power of the agent employed must govern the nature of the product and the quantity of the product obtained must depend upon the velocity at which the total process of reduction occurs. The total process of reduction takes place in two steps: (1) the dissolving of the N_2O with the formation of $(NOH)_2$ and (2) the reduction of the $(NOH)_2$ formed, by the different reducing agents. It is highly improbable that these two reactions will take place at the same rate under varying conditions and the velocity of the total reaction will be dependent upon the rate at which the slower reaction occurs.

In all of the experiments where the concentration of the reducing agent was varied, the acid concentration was very low or zero and the temperature was kept at 20°C. Unless then, the concentration of the reducing agent itself has some effect, the first reaction in the process should take place at constant speed, and the total velocity of the reaction will depend upon the speed of the second reaction. Since the speed of a reaction is proportional to the active mass of the reactants, it would be expected that an increase in the concentration of the reducing agent would increase the velocity of the reaction. Also, an increase in the time of contact should increase the total amount of reduction which occurs. The curves (Fig. 2) show that this is true.

It has already been stated[1] that the decrease in the reduction of NO with $SnCl_2$ at high temperatures is probably due to the decreased solubility. Since nitrous oxide is only sparingly soluble at high temperatures, any increase in the temperature will decrease the amount of N_2O that would be dissolved when equilibrium is reached in the first reaction. This would decrease the concentration of $(NOH)_2$ and result in a decreased percentage of reduction for a given time of contact. Increased time of contact would give increased reduction. The curves (Fig. 3) show that results of this nature were found.

The decreased reduction with increased acidity might be due to any of the following causes: (1) A decrease in the velocity of the reduction of $(NOH)_2$ because of (a) a decrease in the concentration of the Ti^{+++} of Sn^{++} ions due to the repression of the ionization by HCl or (b) a decrease in the reducing power of the $TiCl_3$ and $SnCl_2$ with increased acidity. (2) The acidity of the solution decreasing either the rate of attainment of equilibrium in the formation of $(NOH)_2$, or the equilibrium concentration of $(NOH)_2$.

Experiments No. 9, Table III and No. 7 Table VI show that it cannot be due to decreased ionic concentration. In these experiments, hydrochloric acid was added and then neutralized with sodium hydroxide. The amount of reduction in these cases was much greater than when the equivalent amount of the HCl was present, although the concentration of the Cl^- ion was approximately the same in both cases.

The e.m.f. measurements of the reducing power of titanous chloride decrease with increased quantities of HCl, whereas those for stannous chloride increase under the same conditions (Table IX, and Fig. 5). The case of titanous chloride is what we would expect, while that of stannous chloride at first seems anomalous. Goldschmidt and Ingebrechtsen[2] have shown that the increased reducing power of stannous chloride on nitro bodies with increased acidity is due to the formation of $HSnCl_3$. Since, however, the rate of reduction of N_2O by either $TiCl_3$ or $SnCl_2$ decreases with increased acidity, the change in the reducing power of the solution is not the essential factor.

The controlling factor must be that the increased acidity decreases the rate at which equilibrium is attained in the formation of $(NOH)_2$. If this is the case, then, an equivalent amount of some other acid would have the same effect. This was proved by the use of an equivalent amount of sulphuric acid in experiment No. 8, Table VI and experiment No. 8, Table III. The slightly increased reduction can be accounted for by the difference in the ionization of the acids. Also the presence of some catalyst like platinized platinum should increase the amount of reduction by increasing the rate at which equilibrium in the first reaction is attained. This was found to be the case as shown by experiment No. 10, Table III, and shows that it is the rate of formation of $(NOH)_2$ which is affected by the acid, and not the equilibrium concentration of $(NOH)_2$.

---

[1] Bancroft: J. Phys. Chem., **28**, 488 (1924).

[2] Goldschmidt and Ingebrechtsen: Z. physik. Chem., **48**, 435 (1904).

Since the reducing power of titanous chloride decreases and that of stannous chloride increases with increased acidity it would seem probable that the same reduction product should not always be obtained under all of the conditions under which the experiments were performed. However, as the voltage measurements show, the oxidizing power of the nitrous oxide increases with increased acidity. The total effect of the reaction must be represented by the algebraic sum of these two measurements which is shown by the curves (Fig. 5). It is seen that the total reducing power in the case of titanous chloride and nitrous oxide decreases rapidly at the start and then remains practically constant. In the case of stannous chloride the total reducing power increases rapidly at the start but later the rate of increase decreases. This is probably due to the formation of large amounts of $HSnCl_3$ with increased concentration of HCl.

$$\frac{(HSnCl_3)}{(SnCl_2) \times (HCl)} = K$$

The rate of change of reducing power of stannous chloride solutions will naturally decrease as the concentration of HCl increases.

Since the above mentioned curves do not intersect at any point in the region of the values used in these experiments and since the reducing power of sodium sulphite is less than that of either stannous chloride or titanous chloride, the fact that only one primary reduction product is obtained with each reducing agent is readily explained.

With higher concentrations of hydroxylamine in the presence of an excess of stannous chloride, other experimenters have found[1] that ammonium salts may result. Stannous chloride is therefore capable of reducing hydroxylamine to ammonia, but the low concentrations of hydroxylamine developed in the solutions of this work probably account for the fact that no ammonia was found.

From the fact that the reduction of nitrous oxide to ammonia, hydroxylamine, or nitrogen is dependent upon the reducing power of the salt used, the following is suggested as the mechanism of the reactions.

$$\begin{aligned} N_2O + H_2O &= H_2N_2O_2 \\ H_2N_2O_2 + 2H &= 2\,H_2O + N_2 \\ H_2N_2O_2 + 4H &= 2\,NH_2OH \\ H_2N_2O_2 + 8H &= 2\,NH_3 + 2H_2O \end{aligned}$$

This view was also advocated by Milligan and Gillette.

---

[1] Milligan and Gillette: J. Phys. Chem., **28**, 744 (1924).

Summary

The results of these experiments may be summarized as follows:

1. Nitrous oxide is reduced by aqueous solutions of titanous chloride, stannous chloride and sodium sulphite, with the formation of ammonia, hydroxylamine, and nitrogen respectively.

2. The rate of reduction of nitrous oxide by aqueous solutions of these salts decreases with increase in temperature.

3. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride and stannous chloride decreases with increased acidity.

4. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride is catalyzed by platinized platinum.

5. The rate of reduction of nitrous oxide by aqueous solutions of titanous chloride, stannous chloride and sodium sulphite increases with increase in concentration of the reducing agent.

6. The probable mechanism of the reduction of nitrous oxide has been suggested.

A COMPARATIVE STUDY OF TWO KINDS OF COLORED ROCK SALT*

BY T. E. PHIPPS AND WALLACE R. BRODE

Introduction

Two kinds of colored halite were investigated, the deep-blue naturally occurring variety,—hereafter called "Stassfurt blue halite",—and halite colored by heating in contact with alkali metal vapor at high temperatures,—hereafter called "sodium-colored halite". The blue color of certain Stassfurt halites attracted the attention of Sir Humphry Davy in 1818, and though many researches into the cause of the color have been undertaken since that time[1] a satisfactory explanation is still lacking. The theory which seems to have found most support is the one suggested by Zsigmondy,[2]—that the color is due to colloidal particles of free metal in the halite. This explanation has been accepted by many colloid chemists, notably Siedentopf[3] and Svedberg.[4] Siedentopf studied the Stassfurt blue salt with the ultramicroscope and published patterns of what he believed to be particles of sodium in the halite lattice. Siedentopf's evidence was questioned by Spezia,[5] who failed to find any trace of alkalinity to indicators in water solutions of the blue salt. One or two other investigators agree with Spezia as to the non-alkalinity of such solutions.

Ordinary colorless halite can be colored[6] by heating it in contact with sodium vapor to temperatures above 650°C. This is done most easily by sealing up cubes of rock salt with sodium in an iron crucible with a high-temperature cement and heating in an electric furnace for an hour or more. The colors obtained with different heat treatments will be discussed later in this paper. Siedentopf[7] sealed crystal and metal up in a glass tube, and heated to a temperature 50° to 80° below the boiling point of the metal (680°C. for sodium and 590°C. for potassium). At lower temperatures the vapor pressure of the metal was too low and at higher temperatures he states that the metal distills out of the crystal again and the glass is attacked. Higher temperatures can be used with the iron crucible; on the other hand, temperatures too near the melting point of the halite are not desirable, since only an amber or pale straw coloration is obtainable under these conditions. It is conceded by all investigators that crystals colored in this manner contain free sodium, visible ultramicroscopically, and that their water solutions are alkaline.

---

*Contribution from the chemical laboratory of the University of Illinois.

[1] A complete summary may be found in Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", **2**, pp. 530 et seq. (1922).

[2] "Zur Erkenntnis der Kolloide," p. 58 (1905).

[3] Physik. Z., **6**, 855-864 (1904).

[4] "Colloid Chemistry," p. 67 (1924).

[5] Centr. Min. **1909**, 394-404.

[6] For references see Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **2**, pp. 530 et. seq.

[7] Siedentopf: Physik. Z. **6**, 855-864 (1904).

In general the two types of colored halite behave quite differently toward heat, the Stassfurt blue fading out at about 300°C, whereas the artificial color persists (though faintly) up to the melting point. Nevertheless it is possible to prepare artificially colored crystals which match Stassfurt blue crystals fairly closely both as to visual tint and depth of color; hence it is not surprising that many investigators have supposed that the color is due to the same cause in both cases.

Two lines of study occurred to the authors: (1) an accurate comparison by means of the hydrogen electrode of the alkalinities of water solutions of the two types, and (2) a comparative spectrophotometric study of the two types over the ranges of temperature where color changes occur.

A. Study of the Alkalinity of Water Solutions of the Two Types of Colored Halite.[1]

After several attempts to adapt the Hildebrand and other types of hydrogen electrode to the problem, the electrode shown in Fig. 1 was designed. The Pyrex electrode vessel is of the captive hydrogen type, and combines features of the Clark and of the Bailey vessels. It has the following advantages: (1) it comes to quick equilibrium, (2) it can be stirred simply and effectively by tilting back and forth a few times, thus eliminating complicated mechanical stirring, (3) after the first few rapidly performed steps it is protected from further contamination by the CO_2 of the air, (4) the electrode is easily replaceable, and (5) the trap connection to the saturated KCl calomel half-cell gives steady boundary conditions between the two liquids. The operation of the electrode is as follows:

The vessel (Fig. 1) is completely filled with conductivity water, and while it is held in the position shown in Fig. 1, it is about half filled by downward displacement with purified hydrogen led in through C. A weighed crystal is dropped into the bend, and the ground glass stopper D is seated so as to completely exclude the air. Equilibrium is then quickly obtained between hydrogen, solution, and electrode by one or two minutes of vigorous shaking. Then, with the arm A vertical as in Fig. 1, the stopper D. is removed and connection is quickly made with the saturated KCl calomel electrode (Fig. 2) by slipping the arm B over F and tightly engaging the rubber stopper G,—the arm A still being kept vertical. This puts a slight pressure upon the hydrogen, and when H is opened to the atmosphere, the solution runs up into the trap about half-filling it and resting upon the denser saturated solution of KCl below. The arm A is then turned to a horizontal position (shown in Fig. 2) by rotating the stopper G about its axis.

The E. M. F. of the combination is measured by a Leeds and Northrup Students' Type Potentiometer. Ordinarily, steady readings are obtained within two or three minutes. At the end of the run the hydrogen electrode is disconnected at G, the total volume of the solution is measured, the strap E is flushed out with saturated KCl and another run is begun.

---

[1] This work was done in part by Mr. G. C. Mason. Mason: Thesis for the Degree of Bachelor of Science, Univ. of Illinois (1924).

Measurements were made upon solutions of (1) Stassfurt blue halite, (2) samples cleaved from the colorless portions of large Stassfurt blue specimens, (3) colorless crystals from Navarre, Michigan, (4) crystals from both Stassfurt and Navarre, colored artifically in sodium vapor. Utmost care was taken in the choice of samples of the artifically colored salt for alkalinity tests, to exclude those into which metal might have penetrated by following faults or cleavages or otherwise than by diffusion into the lattice. A large part of any given colored crystal was dissolved away, and only the center, which must appear crystal clear and free of faults, was used for an alkalinity test. Table I gives results representative of more than a hundred such measurements.

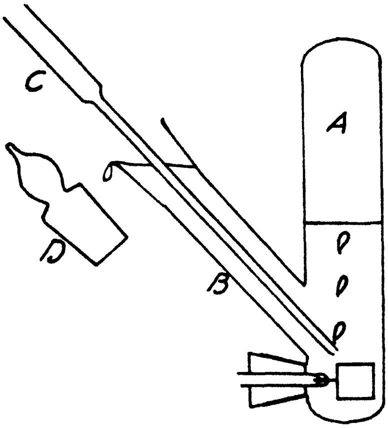


FIG. 1

TABLE I

Dissolved salt	Color	P_H of solution	Normality of free sodium in crystal
Sodium-colored Halite (Navarre)			
1	Blue	8.38	5.2×10^{-4}
2	Pink	7.62	1.6×10^{-4}
3	Pink	8.81	2.3×10^{-3}
4	Green	7.94	1.5×10^{-4}
Halite (Navarre)			
1	Colorless	5.87	Zero
2	”	6.07	”
3	”	6.09	”
4	”	6.02	”
5	”	6.05	”
6	”	6.04	”
Halite (Stassfurt)			
1	Colorless	6.04	Zero
2	”	6.07	”
Halite (Stassfurt blue)			
1	Blue	6.04	Zero
2	”	6.05	”
3	”	6.04	”
4	”	5.98	”
5	”	6.04	”

Solutions of the colorless crystals and of the Stassfurt blue crystals gave practically identical P_H values, while the solutions of the artificially colored crystals invariably gave markedly alkaline solutions,—sometimes 0.001 N or greater. Calculation showed that the maximum concentration of free sodium which (because of limitations of the method) might be conceded to be present in the Stassfurt blue crystal is of the order of magnitude 1×10^{-8} N, or one-hundred-millionth normal. In view of the fact that Kraus has stated that the dilute solution of sodium in liquid ammonia whose *very faint blue* is still just visible, has a concentration of 2.5×10^{-5} or one-forty-thousandth normal, it seems highly improbable that the color in the case of a *deeply colored* Stassfurt crystal could be due to free sodium. There is no case on record, so far as the authors know, where coloring matter in concentrations less than one-forty-thousandth normal has been observable.

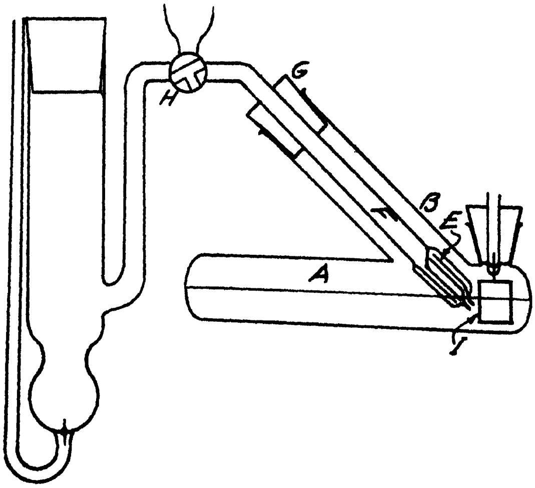


FIG. 2

Clark[1] has pointed out the difficulties which attend the accurate determination of P_H values in unbuffered solutions of salts like KCl in the neutral range; and the uncertainty involved in the "salt error" is well recognized. In this case, however, where we are seeking only comparative data as between solutions of Stassfurt blue and solutions of sodium-colored halite, all such effects may be assumed to cancel. Though the normalities calculated in column 4 can be relied upon to give only the order of magnitude of the free sodium in the sodium-colored crystals, we feel confident that the P_H values in column 3 have a definite comparative value.

Artifically colored crystals were heated just below their melting point, and were found to give alkaline solutions still. Since sodium will dissolve in *molten* NaCl to give a bluish melt, it was hardly to be expected that heating artificially colored halite to its melting point would expel the sodium. Stassfurt blue crystals after being decolorized by heat were found to give the same P_H values in solution as before.

---

[1] "Determination of Hydrogen Ions," 2nd edition, p. 269 (1922).

The results of this part of the investigation seem conclusive against the colloidal metal theory of the color in Stassfurt blue halite. One investigator[1] has stated that *some* Stassfurt blue halite shows alkalinity, implying that most of it does not. Whether or not the blue color is found in some samples which give alkaline solutions, the significant fact remains that a random sample of the characteristic blue Stassfurt halite gave no trace of alkalinity as tested by the hydrogen electrode; whereas under identical conditions artifically colored crystals of approximately the same depth of color, known to contain sodium, showed marked alkalinity in solution.

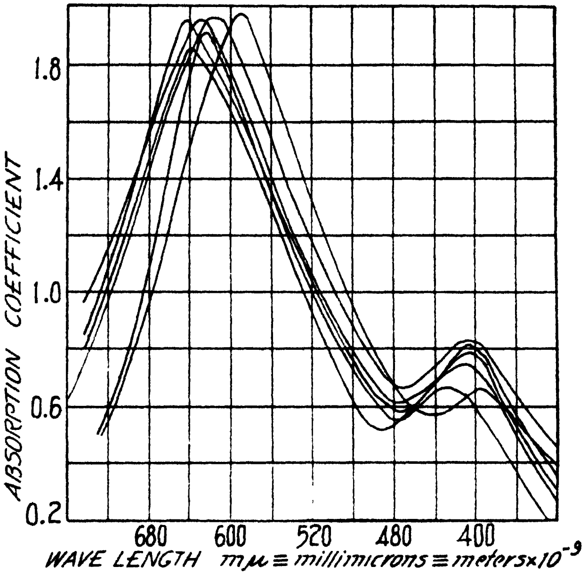


FIG. 3

B. Spectrophotometric Study of the Two Types of Colored Halite

This study was made with a Keuffel and Esser Spectrophotometer. A horizontal, tubular, electrically-heated furnace with end windows of mica was designed to fit into the optical path of the instrument between the light source and the main optical system. The temperature could be raised slowly or rapidly at will, or could be kept constant within less than five degrees. A special holder for the crystal to be examined and for the colorless standard was designed for the furnace. Temperatures up to 350°C were measured with a mercury thermometer introduced laterally into the furnace through a porcelain tube. A chromelalumel thermocouple was used for higher temperatures.

---

[1] Cornu: Neues Jahrb. Min. Geol. 1, 22-58 (1908).

Fig. 3 shows the absorption curves obtained at room temperature for several different samples of Stassfurt blue halite. Two absorption bands are noted, one in the green at 524 mμ, and another more intense band in the red at 640-660 mμ. It is noteworthy that the vibration centers of the bands, though not quite constant, vary within a narrow range only, and the ratio between the intensities of the two bands in all cases is approximately constant.

Fig. 4 shows the progressive shift of the maximum of the principal band which resulted when a Stassfurt blue crystal was slowly heated from room temperature up to 320°C. The maximum first shifts toward the yellow, and at the same time begins to drop. Then, still dropping, it moves back toward the red, and finally back again into the yellow before completely fading out. The S-shaped dotted line indicates the movement of the maximum.

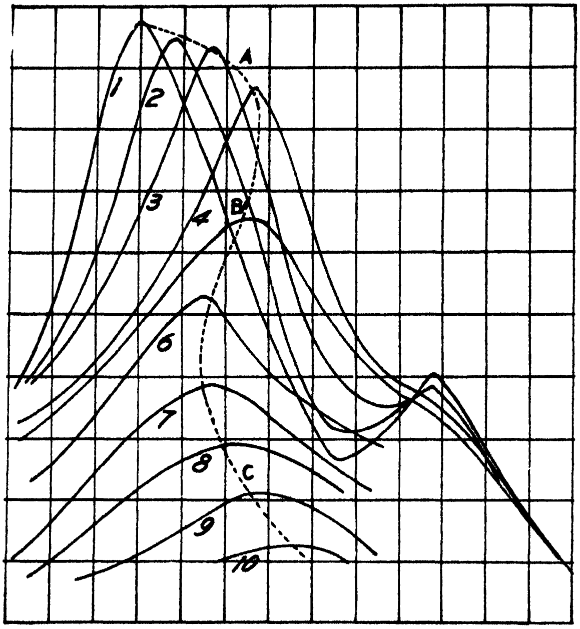


Fig. 4

Fig. 5 shows the progressive shift of the maximum which resulted when a Stassfurt blue crystal was thrust directly into a furnace at 241°C and heated rapidly to 307°C. The maximum quickly shifts without appreciable change intensity to the neighborhood of 589 mμ(± 2 mμ). Then it stops its lateral shifting and drops, maintaining a nearly constant peak at 589 mμ. The behavior toward heat of the Stassfurt blue halite as shown in Figs. 4 and 5 has been checked a number of times and in all cases rapid heating caused the principal band to shift to 589 mμ, followed by rapid fading. In all cases of slow heating there was a shifting of the maximum back and forth between red and yellow, usually in an S-shaped course as shown in Fig. 4. In no case did the band shift further toward the shorter wave-lengths than 589 mμ.

Figs. 6 and 7 show the absorption curves for several samples of rock salt artificially colored with sodium. These crystals show surprising colors and color combinations with varying heat treatment. Often when first removed from the crucible in which they were colored they show a metallic bronze, yellow, brown, green, or smoky gray color, but upon being heated to low redness in air, secondary pink and purplish-blue colors usually appear. It seems probable that the first smoky or cloudy appearance is due to colloidal masses of metal, and that the secondary color development is due to dispersion of the colloidal aggregates by heat. Two principal types of color are evolved by the secondary heating, a purplish-blue and a deep pink. The purplish-blue color (Curves 1, 2, 3, 4, and 5, Fig. 6) exhibits a single broad band having its vibration center in the vicinity of 589 mμ, with a possible secondary inflection in the green in some cases (Curves 3 and 4, Fig 6), reminding one somewhat of the secondary band in the green at 524 mμ for the Stassfurt blue crystals. The vibration center of the principal band is not definite. Nevertheless in all of the crystals studied it lay between 560 mμ and 620 mμ.¶ Curve No. 6 (Fig. 6) which crosses the other curves in the unusual way was obtained from a greenish colored crystal got by suddenly cooling from about 650°C during the operation of coloring.

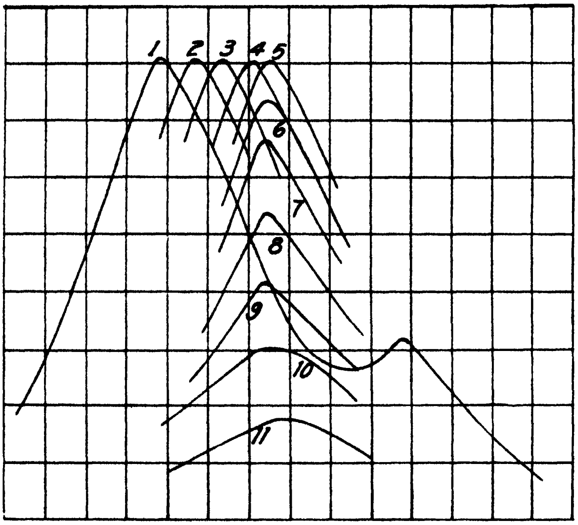


Fig. 5

The other type of color produced by secondary heating is a fine clear pink. Fig. 7 shows absorption curves for this type. The sharpness and intensity of these bands suggest that there is a single definite vibration in this case. It is also interesting to note that when potassium metal is used in coloring halite the same band (No. 3) is obtained as for pink sodium-colored halite. Absorption curves of this pink type are characterized by a sharp intense band at 552 mμ.

It is possible to produce side by side in the same crystal a pink and a purple-blue region merging into each other, by sudden cooling of one edge of a crystal during the secondary heating operation. Usually the pink region will be found deeper in the crystal and the blue next to the surface, though sometimes one meets with a reversal of this order. In general the progression of colors with rising temperature is (1) purplish-blue (2) deep pink (3) amber and (4) pale straw (just below the melting point of the crystal). These are the colors obtained in a cold crystal by heating it to successively higher temperatures and cooling it periodically. When hot a crystal will usually show a color one or two steps lower in the series than when cold; for example a crystal which will show a pink when cold will look purple when hot, and one which is amber when cold will look pink or purplish-pink when hot. The series seems to be irreversible. Thus when a purplish-blue crystal has been heated sufficiently to cause it to show pink when cold, the purple tint when cold cannot be restored by any heat treatment or other treatment. On the other hand, by carefully heating a purple crystal, a part only of the purple modification can be converted into the pink, and beautiful magenta shades can be produced by the blending. The amber color which is obtained by heating sodium-colored crystals to high temperatures matches visually the amber color produced in colorless crystals by exposure to radium emanation. However, we have made no accurate comparison of these two colors.

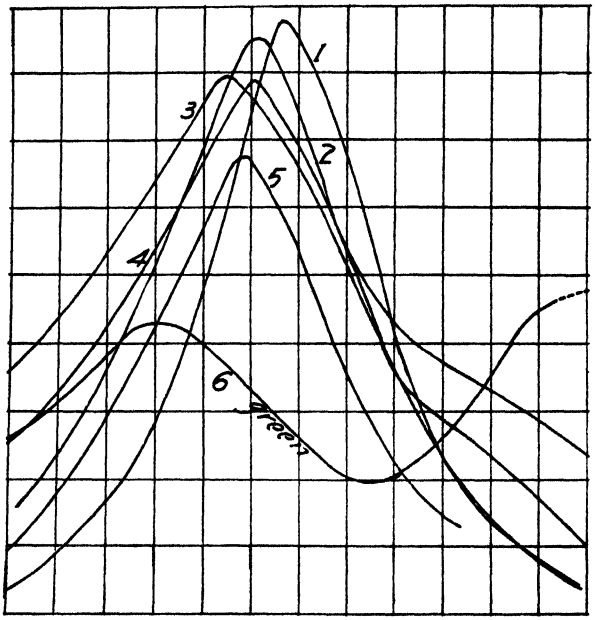


Fig. 6

Fig. 8 shows the effect of heat upon the absorption of a single purple sodium-colored crystal. The band narrows and intensifies to a fairly sharp peak at 589 mμ, and then on fading the peak shifts over toward the shorter wave-lengths (apparently approaching 552 mμ). At the same time the curve shows a secondary inflection at or near 589 mμ, showing the continued presence of a small number of vibrators of this original frequency even at the higher temperature. The sequence of curves with rising temperature, beginning with No. 1 at 310°C, is readily followed in Fig. 8.

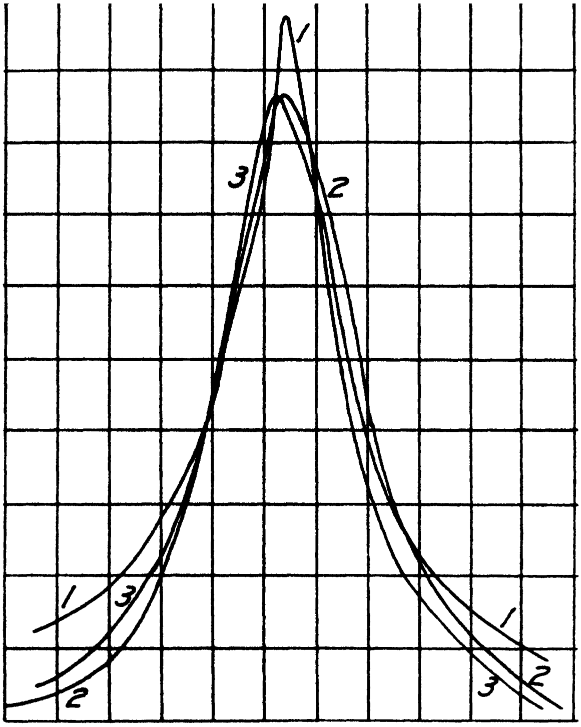


FIG. 7

Fig. 9 shows the effect of heat upon a typical pink sodium-colored crystal. The band moves from 552 mμ over to 589 mμ, maintaining its sharp well-defined character. Then it fades, and during the fading the band appears to shift back and forth between 552 mμ and 589mμ.

A brief comparison of the effect of ultra-violet light upon Stassfurt blue and sodium-colored halite was attempted. Crystals of the two types were exposed side by side for two hours at a distance of 12 inches from a quartz mercury vapor lamp. The sodium-colored crystal (purplish-blue initially) was changed to a pale straw color visually identical with that got by heating such a crystal to a high temperature, and with that produced in a colorless crystal by radium emanation. There was no effect whatever upon the Stassfurt blue. The fading of the latter seems therefore to require vibration of the lattice produced only by temperature.

Discussion

The recurrence of 589 mμ (Figs 4 and 5), the wave-length of the D-line of sodium, as the wave-length at which fading occurs in all Stassfurt blue crystals suggests at once the possibility that the Stassfurt blue may be due to an abnormality in the constraint upon the valence electron at various points in the halite lattice, and that the fading of the color with heat may come from the return of the electron to its normal constraint. If this is the case we may expect the fading at 589 mμ to be coincident with the appearance or intensification of an absorption band beyond the visible part of the spectrum,—perhaps in the ultra-violet.

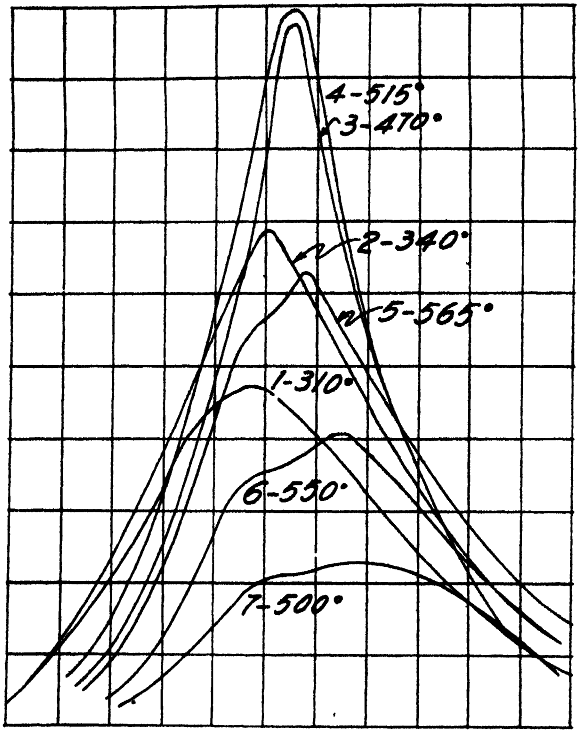


FIG. 8

The theory that electronic displacement constitutes one cause for color in crystals has been clearly stated by Lind and Bardwell[1] and we quote here from the concluding paragraphs of their recent paper. "Certain groups of electrons are displaced by radiation from their normal positions and take up new metastable positions among the atoms. No displacement (or only secondary displacement) of the atom is involved. No change in the crystal lattice as revealed by X-Rays would be expected nor would there by any production of colloidal particles. One or more groups of electrons may be involved. . . It appears to us probable that the color is due to the vibration of electrons in their abnormal positions. . . . Since the crystal is transparent, the color complementary to the one absorbed by the electronic vibration is transmitted. In the metastable positions, under less constraint, the electrons are also freer to take part in electrical conduction and in photo-electric emission under radiative stimulus, and can also return to their normal positions under this stimulus or by that of heat."

---

[1] J. Franklin Inst. 196, 375 (1923).

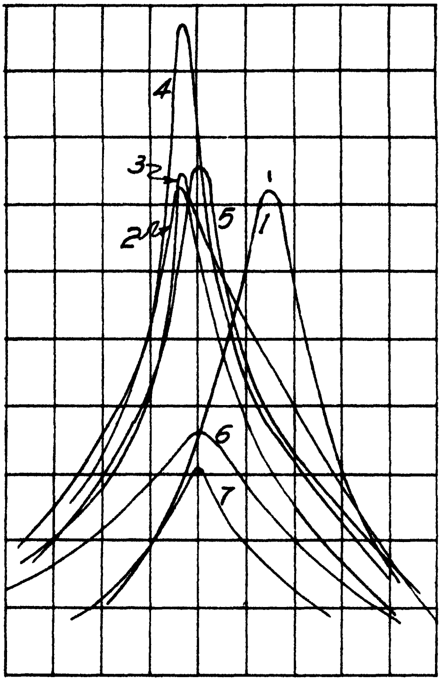


Fig. 9

Without committing ourselves finally as to the exact nature of the Strassfurt blue color, we may seek a general explanation for the rather complex shiftings of the maximum of the principal band with different rates of heating, as shown in Figs. 4 and 5. We shall make the following assumptions: (1) the primary cause of color in the principal band exists in two modifications which we shall call the "650" and the "589". The "650" is stable at room temperatures as low as 190°C undergoes slow transition into the "589". At 300°C the transition is very rapid. We shall speak of the "rate of transition" of the "650" into the "589", and this will be measured by the rate of lateral shifting of the principal band. The rate of transition depends upon the temperature only. (2) The "589" changes into a colorless modification. We shall speak here of a "rate of fading" and this will be measured by the rate at which the principal band drops. If the cause of the color is indeed the electron as suggested above, and if the fading at 589 mμ is coincident with the appearance or intensification of an absorption band in (say) the ultra-violet, then the rate of fading may be determined by the rate at which the electron at the 589 "level" can acquire radiation of the critical frequency necessary to translate its absorption into the ultra-violet. This radiation may come largely from the spectrophotometer light source, or it may be radiation to which the crystal gives rise by virtue of its own temperature.[1] We shall assume then that the slow step which decides the rate of fading is the acquiring of this critical frequency, and that this depends mainly upon temperature and upon radiation from the light source of the spectrophotometer.

With these assumptions in mind, we conclude that with rapid heating (Fig. 5) the transition rate is very much greater than the fading rate, so that all of the "650" changes to the "589" before an appreciable fraction of the "589" can fade. The result is that the peak moves rapidly from 650 mμ to 589 mμ without appreciable dropping (fading). The rate of dropping at 589 mμ is then determined by the rate at which the critical fading frequency is acquired.

With slow heating (Fig. 4), we shall distinguish the following stages as designated by letters on the S-curve:

(A) In this range the transition rate is somewhat greater than the fading rate. During this interval perhaps 75 percent of the "650" undergoes transition, and of this fraction perhaps only 10 percent fades. The maximum of the band does not reach 589 mμ at this stage because of the considerable fraction (say 25 percent) of the "650" which remains unchanged.

(B) The transition rate has fallen below the fading rate. All of the "589" produced in (A) fades and the maximum recedes toward the red where the remaining 25 percent (or less) of the "650" still resists transition.

(C) The temperature is now high enough to force transition of the residual "650", and a complete and rapid transition results. The fading rate is not sufficient instantly to remove all of the "589" thus produced. The result is that the band shifts completely over to 589 mμ and quickly fades out there.

In discussion we have been assuming that a certain fraction of the "650" requires a higher temperature for transition than the rest. Indeed this seems to be the case. In several cases a residual faint blue color has been noticed in a crystal which has been held at a temperature above 300°C for as long as 20 minutes. Everything points to the fact that the "650" is not characterized by a single definite frequency nor by a definite temperature of transition.

The purple sodium-colored crystals (Fig. 6) are characterized by rather broad absorption bands which seem to be the resultant of more than one vibration frequency. It seems probable that in such crystals there is present a small fraction of vibrators absorbing at 552 mμ, and a larger fraction absorbing at 589 mμ. To explain curves of the type of No. 1 (Fig. 8) with its minimum lying well beyond 589 mμ toward the red, we must suppose that some vibrators are present which absorb in the orange red or red part of the spectrum. Perhaps the presence of undispersed colloidal particles of sodium in the purple crystal may account for this absorption in the red and for them broad indefinite character of the principal band. It is significant in Fig. 8 that the broad band with peak about 607 mμ upon heating *intensifies* and shifts to 589 mμ. This intensification of color points to a dispersion by heat of colloidal particles. The shifting to 589 mμ suggests the behavior of the Stassfurt blue crystals, except that the principal band in the Stassfurt blue shifted and dropped at temperatures below 300°C whereas the corresponding change in Fig. 8 occurred at temperatures 200° higher. A further difference is that in the case of Stassfurt blue the principal peak never shifted further than 589 mμ toward shorter wave-lengths, whereas in Fig. 8 the principal band of the sodium-colored crystals shifted at high temperatures well over toward 552 mμ.

---

[1] Experiment showed that a crystal heated above 300°C in the dark for several hours will fade completely, in the absence of any incident radiation from the spectrophotometer light source or otherwise.

In Fig. 7 we undoubtedly have a pure color. The sharpness and intensity of these bands suggests that there is a definite vibration here which might be considered as a resonance band. The identity of the absorption curves of sodium-colored and potassium-colored halite may be explained by supposing that there is an actual replacement of sodium by potassium in the lattice, or by supposing that the color is electronic and a function more of the lattice than of the parent alkali metal.[1]

The effect of increasing temperature upon sodium-colored halite (Figs. 8 and 9) is first to intensify the principal band while shifting it to 589 mμ, and then to fade the principal band while shifting it toward the green. There seem to be two definite vibration centers, at 552 mμ and at 589 mμ. With rising temperature first the 589 vibration is intensified and predominates; then at higher temperatures the 589 absorption band fades and is replaced by one at 552 mμ. It is possible that the change from purplish-blue to pink is due to a change in the crystal structure of NaCl at high temperatures. The fact that two colors predominate and that such complex color results can be obtained merely by variation of the heat treatment indicates that the color is dependent upon an inner equilibrium between two crystal forms in the halite lattice. The surprising change in slope of the temperature-conductance curve of NaCl (when log. specific conductance is plotted against reciprocal of absolute temperature)[2] in the neighborhood of 490°C points to a possible change in crystal form.

In conclusion, the Stassfurt blue is probably due to abnormality in constraint upon electrons which belong properly to the halite lattice. In sodium-colored halite on the other hand the coloring principle is foreign to the lattice, consisting of sodium which may coagulate into colloidal particles in voids of the lattice, or may be dispersed in solid solution, depending upon the heat treatment. Here too the color is due to the electron, but the constraint upon it is distinctly different from that in the Stassfurt blue, being the resultant in a sense of the force of attraction of the parent metal atom and the dielectric forces of the lattice. The irreversible character of the color changes produced in sodium-colored halite at high temperatures suggests that there may actually be a warping of the lattice at high temperatures to accommodate the foreign sodium atoms, with the resulting formation of some subchloride structures in the crystal. X-Ray analysis might be expected to reveal such a condition.

---

[1] Gibson and Argo [Phys. Rev. 7, 33 (1916); J. Am. Chem. Soc. 40, 1345 (1918)] showed that sodium and magnesium gave blue solutions in liquid ammonia having identical absorption spectra. Also they showed that the absorption curves of Na, K, Ca, and Cs in methylamine are nearly identical. The color in all these cases was thought to be due to solvated electrons existing more or less independent of the parent atom.

[2] Data of v. Seelen: Z. Physik, 29, 125 (1924), corroborated by unpublished work of one of the authors.

Summary

(1) Solutions of Stassfurt blue and of sodium-colored halite were tested for alkalinity in a special type of hydrogen electrode vessel here described. The former gave no measurable alkalinity. This throws serious doubt upon the theory that the Stassfurt blue color is due to colloidal sodium. Sodium-colored halite under the same conditions invariably showed marked alkalinity.

(2) Spectrophotometric data at room temperature and over wide ranges of temperature show that there is a distinct difference between the two colors.

(3) It is suggested that the Stassfurt blue is an electronic color, and a tentative explanation of the behavior of its absorption curves with heat is given.

(4) Speculation as to the nature of the two predominant colors in sodium-colored halite is indulged in.

BLUE WOOD[1]

BY WILDER D. BANCROFT

In 1903 von Schrenk[2] published a bulletin on the 'bluing' and the 'red rot' of the western yellow pine, which turns out to be concerned with a question of structural color.

"Very soon after the attack of the bark beetles (*Dendroctonus ponderosae*) the wood of the pine turns blue. The color at first is very faint, but it soon becomes deeper. . . . Lines of color extend in from the bark toward the center of the tree, and increase rapidly in intensity until the colored areas stand in sharp contrast to the unaffected parts. The color appears in small patches at one or more points on the circumference of the wood ring. At first it is a mere speck, but this gradually spreads laterally and inward, eventually forming triangular patches on cross section. The color likewise spreads up and down the trunk from the central spot. As the time passes after the first attack of the beetles, several color patches may fuse. . . . The intensity of the color may vary considerably on the two sides of one and the same trunk. After a certain period of time the whole sapwood will have a beautiful light blue-gray color. The wood which adjoins the inner line of the 'blue' wood is of a brilliant yellow color which contrasts sharply with the blue outside and the straw yellow of the heartwood. . . .

"The blue color of the wood is due to the growth of a fungus in the wood cells. The staining of wood due to fungi has been known for many years, especially the form known as 'green wood' (*bois verdi*). In Europe this green coloration attracted the attention of foresters and investigators as early as the middle of the last century, and a number of descriptions and discussions appeared from time to time (particularly in France), in which an attempt was made to account for this phenomenon. A green dye was extracted from the wood, which at one time was thought to be valuable because of its absolute permanency. Various dicotyledonous woods showed the green color; among others, beech, oak, and horsechestnut. In spite of numerous investigations, the causes of the green color and its relation to the wood remained comparatively obscure until recently when Vuillemin[3] published an extended account showing that one form of the green color was due to the growth in the wood of one of the Discomycetes, *Heliotum aeroginosum*. . . . Without going into details, Vuillemin established the fact that the green coloring matter called xylindeine, is formed by the hyphae of *Helotium aeroginosum*, and that the presence of these green-colored hyphae gives the green color to the wood. The wood fiber itself remains colorless. The xylindeine is soluble in alkalies and can readily be extracted. The wood fiber is not destroyed, but remains intact. . . .

---

[1] This paper is a necessary consequence of experiments supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Bureau of Plant Industry, Bull. No. 36 (1903).

[3] Bull. Soc. Sci. Nancy, (2) **15**, 90 (1898).

"In Europe the blue color of pine wood was first noted by Hartig[1], who refers briefly to the fact that a fungus (*Ceratostoma piliferum* (Fr.) Fuckel) is the cause of bluing in coniferous wood, especially of pine trees which have been weakened by caterpillars, and of firewood. He states that the hyphae of this fungus, which are brown, grow rapidly into the trunk through the medullary rays and that they avoid the heartwood, probably because of its small water content. The blue color of coniferous wood in this country is probably caused by the same fungus referred to by Hartig, although it seems necessary to refer to it under a different name (*Ceratostomella pilifera* (Fr.) Winter)."

"The spores of the 'blue' fungus are probably blown about by the wind in countless thousands, and at the time of the beetle attack in July and August some of the spores lodge in the holes made in the bark of the living pine tree by the bark and wood-boring beetles. The atmosphere of these holes is kept constantly moist by the water evaporating from the trunk. In these holes the spores can germinate within a day after falling there. . . . The hyphae grow into the bark tissues and into the cambium, and from these they enter the cells of the medullary rays. . . . The hyphae are at first colorless, very thin-walled, and full of vacuoles and oil globules. . . . The older turn brown and with the first sign of the brown color in the hyphae the bluish coloration of the wood begins."

"So far as known to the writer, no attempt has ever been made to explain the nature of the blue color of coniferous woods. The color is a difficult one to define. A number of the writer's artist friends who were called into consultation pronounced it a blue gray, approaching Payne's gray. Freshly cut wood looks decidedly blue, but as the wood dries the color fades somewhat and dry wood is mouse gray. . . . There are two possible explanations as to the cause of the so-called blue color: (1) The wood may appear colored because of the presence of the colored fungus threads in the wood. The mass effect of such colored threads might make the wood appear colored. (2) The wood might be colored by a pigment or stain formed either by the fungus or as a result of the fungus growth in the wood, and this pigment might stain the walls of the wood fibers.

"The first explanation holds good for the 'green' wood. Here a pigment is formed in the hyphae and fruiting bodies of the fungus, and it is because of the presence of the green-colored bodies in the fungus threads, according to Vuillemin, that the entire wood looks green. Careful examinations made of the 'blue' wood by persons trained to observe colors, called into consultation by the writer have led to somewhat conflicting results, and it is therefore thought inadvisable in the present stage of the investigation to enter on a lengthy discussion of the color subject. A number of facts may be stated, however. Examinations of the wood fibers of sound and 'blue' wood showed that it was possible in most instances to distinguish between the sound and the

---

[1] "Lehrbuch der Pflanzenkrankheiten," 75, 106 (1900).

'blue' wood. The walls of the sound wood look somewhat darker (with a suggestion of purple) than the blued fiber. This method of examination, with high magnification, is a rather uncertain one, however, for the refraction caused by the containing liquids, which are purplish, and of light falling from a blue sky, is apt to show very faint traces of color which do not belong to the wood. It may be stated definitely that the fibers of the 'blue' wood show no indication whatever of any color element seen in the wood en masse.

"The hyphae constitute the only color element present in the 'blue' wood which could not be detected in the sound wood. These are present in the medullary rays and adjacent cells, as described above. These hyphae are pale reddish-brown, a color which may be obtained by taking a pale tinge of warm sepia. This color is very distinct and stands out in sharp contrast to the surrounding yellow wood fibers. How these brown hyphae could make a blue gray or a mouse gray it is difficult to understand, for no density of such a brown, even in combination with straw yellow (of the wood fiber) could possibly produce blue gray. It would therefore seem probable, or at least possible, that there is some pigment with a blue element in the 'blue' wood which is so faint that its detection in thin microscopic sections becomes almost impossible.

"All efforts to extract any color of a blue nature from the wood have so far failed. Extracts of blued wood with ether, alcohol, benzol, chloroform, alkalies, and acids gave evidence that changes of some sort had taken place in the wood fiber, for the extracts of sound and 'blue' wood differed materially in nearly every instance. No signs of any blue or blue-gray color were obtained."

Last year Mr. von Schrenk was good enough to call my attention to his bulletin and to send us a sample of 'blue' wood, suggesting that perhaps the color was a structural one and not a pigment color. The sample of wood was not as blue as some pieces. It was blue only in courtesy, Mr. von Schenk's mouse gray being a better description. The sample was examined by Mr. Mason of the Cornell Laboratory, who reports that the so-called blue is a poor form of the Tyndall blue. It has already been pointed out[1] that one can get blue-grays to grays by mixing graphite or lampblack with zinc oxide. Mr. Mason found that the color of the wood could be duplicated exactly by putting a very thin wash of India ink on the unchanged wood.

Some one, whose letter I have filed so carefully that I cannot at present lay my hands upon it, sent me a sample of really blue wood from somewhere on the Mississippi River. The color was a pigment color due to vivianite, a somewhat oxidized ferrous phosphate. Mr. Mason recognized the material as identical with the 'blue roots' described by Dudley[2] in 1890.

"While making the preliminary survey of the Cumberland river from Nashville to its mouth . . . Assistant Engineer C. A. Locke discovered some 'blue roots' embedded in a stratum of clay which had been exposed in the bank made by the erosion of the waters in cutting out the channel of the river. The locality was about two miles above Eddyville, Ky. The stage of the river was about six feet above low water mark, and the stratum containing the roots was about two feet above the surface of the water or eight feet above low water. The stratum is exposed therefore only for a limited season each year. . . .

---

[1] Merwin: Proc. Am. Soc. Testing Materials, **17** II, 503 (1917); Bancroft: J. Phys. Chem., **28**, 25 (1924).

[2] Am. J. Sci. (3) **40**, 120 (1890).

"Four of these 'roots', more or less perfectly preserved, were handed to me. They were from one-half to two centimeters thick and six to twelve long. The blue mineral which has almost wholly replaced the woody fiber of the roots is of a deep blue color resembling cobalt-blue but somewhat darker, and of a duller hue. It is earthy and very friable. There is no evidence of structure, and the specimens seem to be casts of the original roots, formed gradually as decay proceeded."

The mineral was extracted and analyzed with the following result: water given off at 100°, 10.59%; water given off at 230°, 7.24%; alumina 17.74%; ferric oxide, 9.35%; ferrous oxide, 24.58%; lime, 0.59%; magnesia, 0.43%; P_2O_5, 27.71%; insoluble matter, 1.84%. "When the water was driven off at 100°, the residue had a dull green color resembling chrome oxide. After heating to 230° until all of the water was eliminated, the color was light brown. In a desiccator, over sulphuric acid, the mineral gradually lost water and for several days became green. This occurred more rapidly of course if the air in the desiccator was exhausted."

Dudley concluded that the ferrous iron in the mineral was combined with the phosphate to form vivianite, $Fe_3(PO_4)_2 . 8H_2O$. The balance of the material has the formula $Al_6Fe_2P_4O_{22} . H_2O$, "which resembles an almost dehydrated double molecule of turquoise, $Al_8P_4O_{22} . 10H_2O$, in which one molecule of Fe_2O_3 has replaced one of Al_2O_3. The mineral was so earthy and friable that sections could not be cut and therefore microscopic evidence is impossible."

The blue of the wood is therefore a structural color and the blue of the roots a pigment color.

Cornell University

THE THERMIONIC PROPERTIES OF SOME MIXTURES USED AS CATALYSTS IN THE SYNTHESIS OF AMMONIA

BY C. H. KUNSMAN

The synthesis of ammonia from N_2 and H_2 in the presence of a catalyst is generally considered to be an example of chemical action on a surface, or surface catalysis. In order to obtain further information as to the nature of such surfaces, both their chemical and physical properties are under investigation at the Fixed Nitrogen Research Laboratory. What follows has to do entirely with one property of the surface, namely, the thermionic emission of charged particles as a function of the temperature of the surface. Since the temperature of the catalyst is such an important factor in the synthesis process, any information as to the nature of the catalyst surface that can be obtained under the same temperature conditions of operation of the catalyst will be especially valuable.

The ammonia catalysts studied were made by fusing a mixture of very pure artificial magnetite, with about 1% Al_2O_3 and about 1/2% of an alkali or alkaline earth salt, usually the nitrate, in a resistance furnace where the mixture itself furnishes the resistor[1]. The reduced mixture probably consists largely of metallic iron with the oxides of aluminum and an alkali or alkaline earth metal oxide which was introduced in the original mixture. The iron is usually considered the catalyst, and the added materials, the promoters.

The property of small amounts of an added material of greatly increasing the chemical activity of the mixture is quite common, and is not confined to ammonia catalysts. There are a number of instances where the alkalies are especially good promoters. For example, a small amount of an oxide of an alkali or an alkaline earth metal greatly enhances the catalytic activity of the iron-ammonia catalyst containing a refractory oxide. The "synthol" catalyst[2] consists of iron filings impregnated with a strong alkali, as KOH or Rb_2CO_3. Strong alkalies are also added as promoters in some water gas catalysts. It is very likely that the effect on the catalyst materials of the alkali promoter is specific and may indicate a common source of catalytic activity; so that any information that can be obtained from the ammonia catalyst mixture, in relation to the alkali promoter, may contribute to the knowledge of catalysis in general.

If the so-called "surface catalysis" is strictly a surface condition, we are very limited in our present choice of methods of investigation. The fact that the thermionic emission from hot surfaces is largely, if not entirely, a surface effect, and is so very sensitive to minute traces of foreign material on the surface, suggests its use in the study of "promoters" and "poisons" as applied to surface catalysis[3].

---

[1] Larson and Richardson: Ind. Eng. Chem., 17, 971 (1925).

[2] Fischer and Lessing: "The Conversion of Coal into Oils," (1925).

[3] Langmuir and Kingdon find the electron emission of tungsten to be increased by a factor of 10^{20} at 800°K, in presence of a layer of caesium, and to be decreased by a factor of 10^6 in the presence of a layer of oxygen at 1500°K.

This paper will deal largely with the total positive thermionic emission from the surface of the catalyst mixture. The discussion of the exact nature of the emission and its possible bearings on catalysis will be considered at a later time.

Thermionic Properties of Surfaces

Guthrie, in 1873, observed that a hot iron ball at atmospheric pressure emitted positive electricity. O. W. Richardson, in 1902, showed that the equation (1) $I = AT^{\frac{1}{2}} \epsilon^{-b/T}$, satisfied the emission of electricity by heated metals. In this equation, I is the saturation current, positive or negative, T the absolute temperature, A and *b* constants, A representing the current emitted per unit area of hot surface. The *b* constant can be expressed in the form $b = \varphi e/k$, where φ is the equivalent work function in volts, *e* the unit electric charge, 4.774×10^{-10} e.s.u., and *k* the Boltzman gas constant, 1.372×10^{-16} ergs per degree. From the relation $b = \varphi e/k$, we find that *b* in degrees kelvin can be expressed in volts by dividing *b* by 1.16×10^4. φe is the work required to liberate a singly charged particle from the surface; where φ is referred to as the equivalent voltage of the work function. Equation (1) will be used in a consideration of the experimental results, and the corresponding value of φ will be thus obtained. Another method of determining the work function for the electron emission from hot surfaces is the calorimetric method. In this method the amount of cooling of the surface due to the vaporization of charged particles is measured.

Apparatus and Method of Observation

The apparatus and technique employed in these studies are the same as employed in vacuum tube and similar low pressure work. The pumping system consisted of an oil pump connected in series with two mercury vapor condensation pumps. Observations were made at pressures of 10^{-6} mm. of Hg and less, on a well degassed system.

The total positive thermionic emission of the following mixtures containing the materials as given will be considered: No. 216—Fe, Al, Cs; No. 740—Fe, Rb; No. 920—Fe, K; No. 571—Fe, Na; No. 260—Fe, Mg; and No. 319—Fe, Al, Ca.

In the first experiments, the partially reduced catalyst granules were placed in a platinum basket (c) and mounted in a tube as shown in Fig. 1. P is the collecting cylinder surrounding the catalyst and tungsten filament. F was used to heat the cylinder to a red heat on degassing the system and to heat the catalyst to the proper temperature by electron bombardment. The process of degassing by electron bombardment is accomplished by raising F, which is earthed, to a sufficient temperature, 2300°C. with a positive potential of about 500 volts to the cylinder (P).

By means of a series of switches, the parts of the tube could be shifted from the heating system to the emission collecting system. Due to the large mass of catalyst granules in comparison to the size of the 6 mil tungsten filament, the filament would cool to below visible before the temperature of the catalyst had appreciably changed. With this system on September 10, 1924, positive ion currents up to 6 × 10^{-7} amp. at a temperature of about 500°C were measured from a Fe-Al-Cs oxide catalyst. The negative or electron emission at these temperatures was negligible, never more than 1/100 of the positive ion current.

Fig. 2 is a sketch of the next tube used. The essential feature is the enclosed spiral, tungsten filament F_1, which heated the enclosing platinum cylinder by radiation and the catalyst by conduction; thus enabling the catalyst to be heated at any temperature continuously. F_2 is a filament used for degassing the collector (P). F_3 is another tungsten filament so placed as to collect some of the positive ions or material vaporized from the catalyst. From this system, observation of the positive emission as a function of the temperature was made and found to obey Richardson's equation. By measuring the temperature of the hot catalyst by an optical pyrometer, and substituting in equation (1) approximate values of φ_+, the work function of the positive ions, were obtained. The unevenness of the temperature of the catalyst granules made precision measurements of φ_+ impossible.

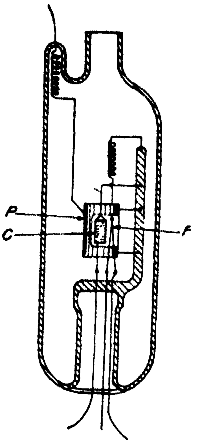


FIG. 1

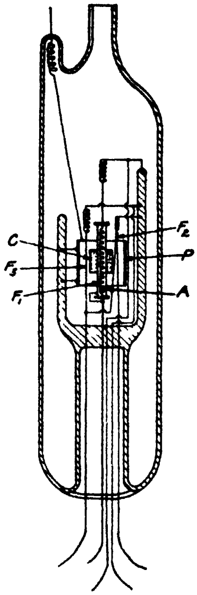


FIG. 2

Nature of Positive Ions

Since the vaporization of positively charged particles took place from a mixture of partially reduced Fe, Al and Cs oxides at relatively low temperatures (below visible) one would no doubt first try to identify the charged particles with the caesium. The property of small traces of the alkali and alkaline earth metals or their oxides of greatly increasing the electron emission of platinum or tungsten, was used in this test[1].

The tungsten filament, F_3 (Fig. 2) was first raised to about 2400°C, so as to remove any impurities from the surface. A test showed that no electrons (currents less than 1 × 10^{-10} amp.) were emitted at 900°C and below. However, after heating the catalyst for a short time and testing the emission from F_3, electron currents as large as 10^{-7} amp. were observed. At temperatures of the filament corresponding to an appearance of the surface of "just visible" and below, tests showed that at a given temperature the magnitude of this negative emission depended upon the length of the time the catalyst was hot, and also on the potential of F_3. For example, if F_3 was at a positive potential with respect to C, the active material collecting on F_3, as measured by the electron emission, was very much smaller than when the filament was negative, with respect to C. This shows that most of the active material carries a positive charge. The increase in emission from F_3, when at a positive potential with respect to C, shows that neutral or negative charged particles may reach F_3. It is difficult to decide whether these particles come from the hot surface directly or from other parts of the tube after having lost their positive charges. However, the amount of uncharged atoms was relatively small in comparison to the positively charged atoms. Hence, we must conclude that at these temperatures the vaporization from the hot surface consists largely of positively charged atoms.

---

[1] Davisson and Pidgeon: Phys. Rev., **15**, 553 (1920); Langmuir and Kingdon: Science, **57**, 58 (1923); Proc. Roy. Soc. **107A**, 61 (1925).

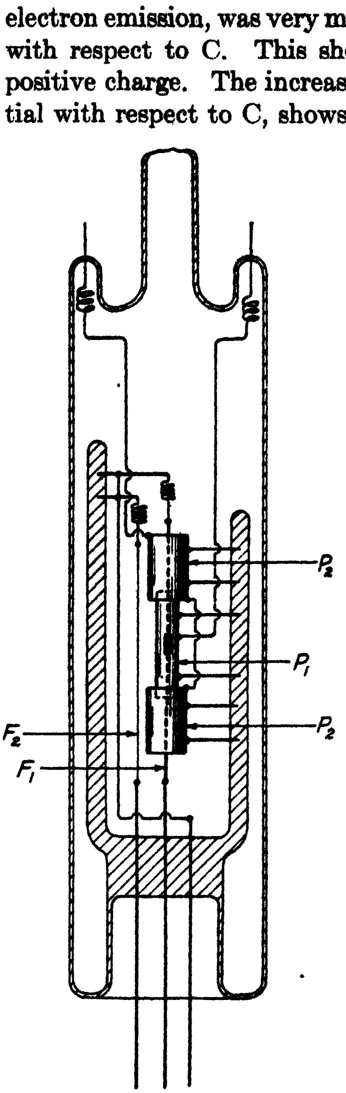


FIG. 3

The effect of caesium on increasing the electron emission on tungsten was investigated in a separate system in the presence of caesium vapor and gave results very similar to those observed for F_3, previously discussed. Quantitatively, the increase was in good agreement with the results reported by Langmuir and Kingdon. It would seem, therefore, that we are justified in concluding that the observed positive currents from a Fe-Al-Cs oxide mixture are largely due to positively charged Cs atoms.

Coated Strip Apparatus

The coated strip form of anode has considerable advantages over the other forms of anodes previously described. It is quite simple to prepare and is very uniform in temperature. While the unreduced mixture can be coated, the reduced mixture can be coated more satisfactorily.

The process consists of grinding the mixture to a very fine powder (300 mesh or lower), similar to the preparation of a specimen for x-ray analysis by the powder method. The powder is then mixed with paraffin and heated until the paraffin melts. The platinum strip is then raised to a sufficient temperature to melt the paraffin. By passing a glass rod covered with the paraffin mixture back and forth over the strip, a uniform layer is obtained. The temperature of the platinum strip was then raised to about 900°C, for a sufficient time (a few minutes) to insure a firm attachment of material to the platinum. This process may be repeated a number of times until the desired thickness of coating is obtained. For some mixtures it was found that a more satisfactory coating could be obtained if the process was carried out in an atmosphere of nitrogen. The coated filament should be mounted in place and the coating reduced by passing hydrogen over the surface, while at a dull red temperature.

A coated strip was mounted as F_1 in Fig. 3; The collector (P) is divided in 3 parts with separate leads to the middle and end parts. This enables the thermionic current to be measured from the middle section (P_1) which surrounds the part of the filament which is at a uniform temperature. Due to the cooling effect of the leads, the ends of the filament are at gradually decreasing temperatures. F_2 is a tungsten filament used to degas the metal parts. Unless otherwise stated, the results which follow were obtained from coated strips.

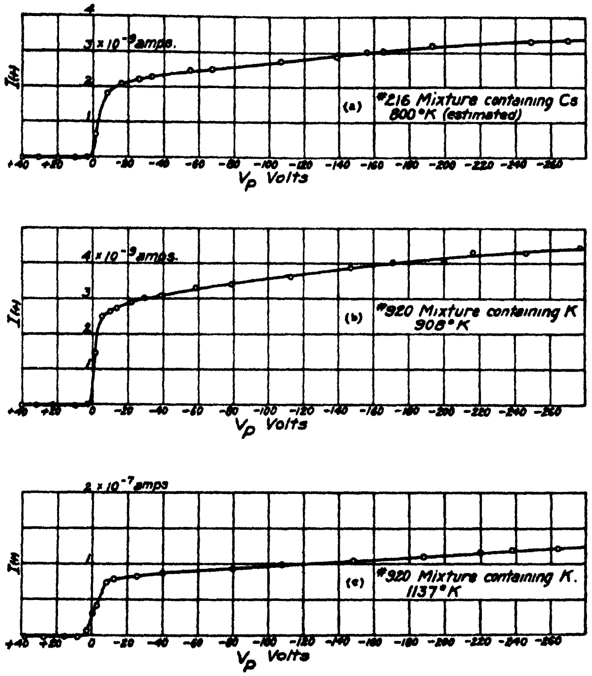


FIG. 4

Experimental Results

If F_1, Fig. 3, is kept at a given temperature and the potential to the collector P varied from a positive through zero to a negative voltage, curves similar to those of Fig. 4 will be obtained. The negative current at these temperatures is practically zero in comparison with the positive currents. In Fig. 4 we have three curves for different temperatures:—(a) a caesium promoted catalyst at 800°K, and (b) and (c) a potassium promoted catalyst at 908°K, and 1137°K, respectively, as determined by an optical pyrometer. The reason the curves do not flatten out or show a saturation current at the higher voltages is no doubt due to the roughness of the surface, so that the added voltage draws a few more ions to the collector. Curves of this type are quite reproducible after a steady state of the hot surface has been reached. The amount of the positive ion currents depends on the mixture and the previous heat treatment. The unreduced material gives some ions but many more are obtained from the reduced mixtures. In general, the magnitude of the positive ion current at a given temperature depends upon the alkali or alkaline earth metal or oxide which has been added as promoter. The temperature at which the first positive ion current, 1×10^{-10} amp. is detected is lowest for a Cs promoted catalyst, followed by Rb, K, Na, Mg and Ca, with increasing temperatures. In the case of a Cs or a Rb promoted catalyst, appreciable positive ion currents are observed at temperatures where the surface was below visible in a very dark chamber.

In all of these tests, the pressure in the system enclosed by a liquid air trap was 10^{-6} mm. of Hg or lower, as measured by an ionization manometer. The system was being evacuated during the course of the experiment. However, no appreciable difference was observed in the results when the pumping system was separated from the test system by means of a mercury trap. Likewise, no increase in pressure was observed in the test system.

Positive Emission—Power Curves

A very convenient method of representing the emission characteristics from a hot surface is shown in Fig. 5.

Dr. C. Davisson[1] has chosen the coordinates, so that, if the emission varies as a function of the temperature as given by equation (1), and the thermal radiation from the coated surface varies as the fourth power of the absolute temperature, a straight line relation exists between the emission from the surface and power supplied to the hot surface.

We have in Fig. 5, the observed positive ion emission from the surface plotted against the watts (amperes × volts) supplied to the hot anode. Straight line relations were obtained as shown by the curves. The observed points for the magnesium-promoted catalyst are shown as dots for increasing heating currents and dots encircled for decreasing currents. The corresponding temperatures for the mixtures for the curves of Fig. 5 were approximately as follows: Cs "below visible" to 1200°K; Rb "below visible" to 1180°K; K "dull red" to 1180°K; Na "dull red" to 1220°K; Mg "dull red" to 1190°K; Ca "red" to 1270°K. This is the order one would expect from the vapor pressure of these elements. Caesium vaporizes from the surface as positive charged Cs ions more rapidly and at lower temperatures than K.

It should be mentioned at this time that in the case of the alkali metals, if the temperature of the material is too high, there is a falling off of positive ions at these high temperatures, and the linear relation no longer holds and the curves for increasing and decreasing heating currents do not coincide.

---

[1] "Thermionic Vacuum Tubes", p. 82; van der Bijl: J. Optical Soc., 8, 79 (1924).

The plots, Fig. 5, represent the emission from approximately one square centimeter of surface. The surfaces of the respective anodes were as nearly the same as they could be made conveniently.

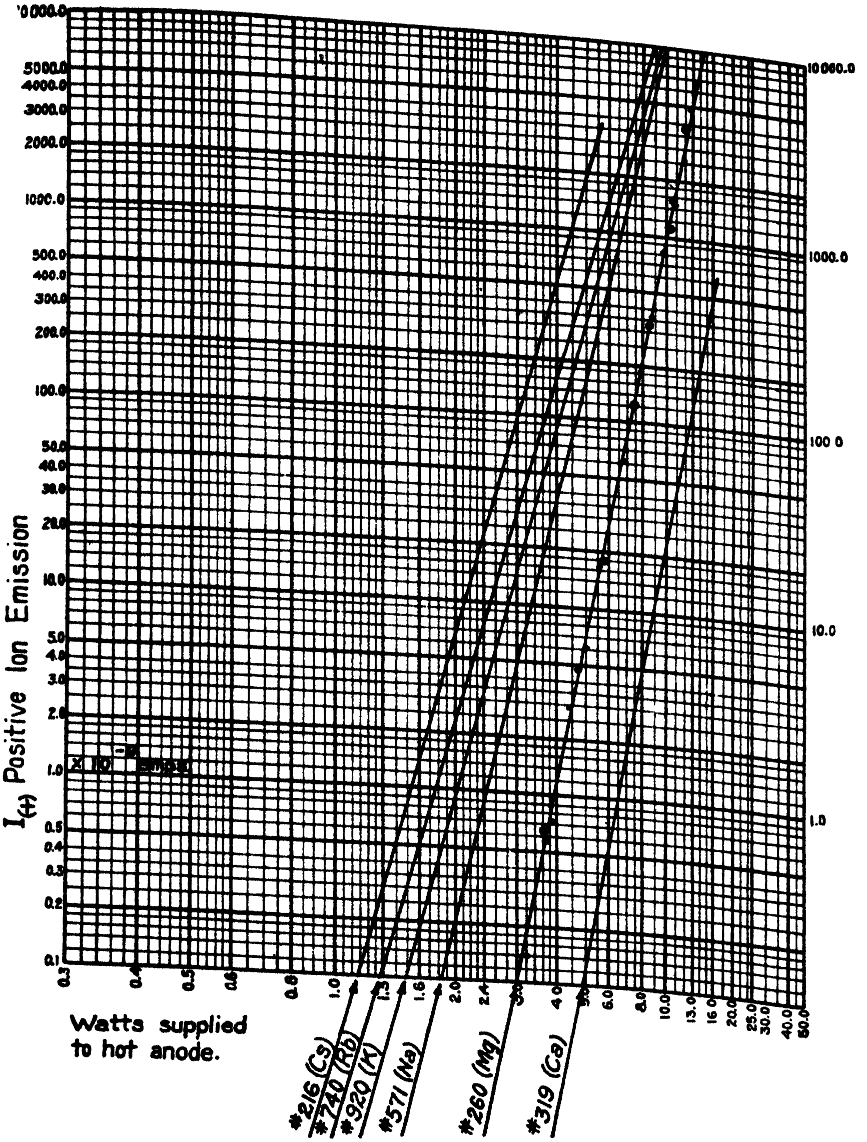


Fig. 5

Determination of φ_+ for K and Cs

Since a linear relation exists for the positive ion emission and the watts delivered to the coated strip, as shown by Fig. 5, we know that the equation (1) $i = AT^{\frac{1}{2}}\epsilon^{-b/T}$ holds through the corresponding range of temperatures. If the temperature is known, the constants A and b, or the equivalent φ, of the equation can be evaluated. The accuracy with which φ_+ can be determined depends upon the measurement of the temperature T. As our chief interest is in a relative definition or comparison of the surfaces of the various mixtures in comparison to their chemical or catalytic activity, no great accuracy is claimed in these values of φ_+. The temperatures are as accurately determined as could be measured in a well darkened chamber by means of a Leeds & Northrup optical pyrometer, calibrated by the Bureau of Standards. The positive ion current I_+ could be very accurately determined for any temperature by a Leeds & Northrup high sensitivity galvanometer.

Equation (1) can be expressed in the form $\log i_+ = \text{const.} + 1/2 \log T - b/T$. In Fig. 6 and 7, the $\log i_+/1/2 \log T$ is plotted against $1/T$. The slope of the line is $-b \log \epsilon$, from which φ_+ is calculated[1].

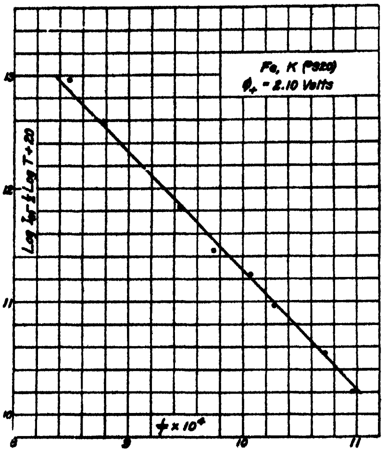


FIG. 6

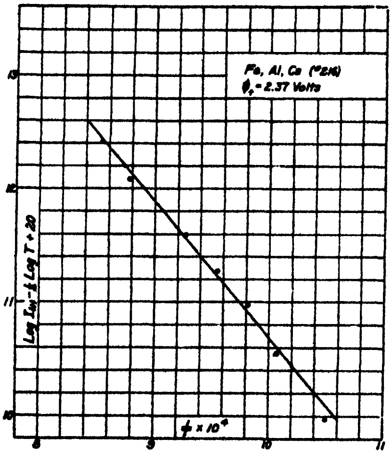


FIG. 7

φ_+ has been found to vary considerably with the mixture and gas treatment of the surface. However, after a preliminary heat treatment, consisting of glowing the filament for some time in a vacuum, consistent values of φ_+ are obtained which can be reproduced from one day to the next. Fig. 6 represents the curve from a K promoted catalyst. In this case, $\varphi_+ = 2.10$ volts, is the equivalent work function in volts for the vaporization of a positive potassium ion from the surface; Dr. H. A. Barton at Princeton, having found that this mixture emitted largely singly charged positive potassium ions[2]. Fig. 7 gives a similar curve for a Cs-promoted catalyst. From the magnitude of the effect of the vaporized atoms on increasing the electron emission of tungsten, we conclude this value of $\varphi_+ = 2.37$ volts is the work function in volts for the vaporization of positive Cs ions from the hot surface.

---

[1] Kunsman: Phys. Rev., **25**, 892 (1925).

[2] Science, **62**, 270 (1925).

Structure of Mixture and Cause of Positive Ion Emission

The recent work of Wyckoff and Crittenden[1] gives us considerable information as to the structure of the mixtures under consideration. One effect of promoters, Al_2O_3 and an alkali metal or alkaline earth metal oxide, is to inhibit the growth of large crystals. An estimate of the size of the crystals in the reduced material is given as lying between 1×10^{-6} cm and 1×10^{-8} cm, where the dimensions are the average length of an edge of a crystal taken as a cube. Another interesting result is that the promoters do not show up in the form of a solid solution or give x-ray diffraction patterns; therefore, their exact form and structure in the mixture are not known. The conclusion drawn was that the promoters, Al_2O_3 and K_2O exist in the reduced mixture as finely divided and uniformly distributed between the Fe crystals.

With this picture of the catalyst material, it is quite easy to see how a diffusion and vaporization from the surface may take place, as a function of the temperature; as it is now generally understood that diffusion takes place largely along interfaces between crystals[2]. With the small crystals there are ample channels for considerable diffusion at the lower temperatures. However, at the highest temperatures for some mixtures, a considerably less positive ion current was observed than would have been expected from Richardson's equation. This is no doubt due to the fact that the diffusion of alkali metal to the surface is too slow for what could vaporize from the surface at these temperatures, according to the vaporization equation.

The same explanation as advanced by Langmuir and Kingdon[3] for caesium in contact with hot tungsten, seems to explain why the alkali metal vaporizes from the surface as positive ions instead of neutral vapor. The electron "affinity" of the surface mixture is greater than the affinity between the alkali metal atom and its outer or conduction electron, so that when vaporization of the alkali metals takes place from the surface, the vaporization is in the form of positive charged ions, instead of neutral vapor. This was shown by experiments where the work function φ_- for the electrons, gave values higher than φ_+ for the positive ions.

Conclusions

1. The fused mixtures of iron oxide containing an alkali or alkaline earth metal oxide and in some cases aluminum oxide, are good emitters of positive ions. The reduced mixtures which are good catalysts for the synthesis of ammonia are considerably better emitters than the unreduced mixtures.

2. The negative or electron emission from the surfaces at these temperatures was very small in comparison to the positive ion emission.

3. The surface of the fused mixture may be defined in terms of φ_+, the equivalent work function in volts of the vaporized positive ions.

---

[1] J. Am. Chem. Soc., **47**, 2866 (1925).

[2] Geiss and Liempt: Z. Metallkunde, **16**, 317 (1924).

[3] Science, **57**, 58 (1923); Proc. Roy. Soc., **107A**, 61 (1925).

4. The catalyst mixture, and therefore, the catalyst surface, is changing at a rate depending on the temperature, due to the vaporization of the alkali which vaporizes in the form of positively charged ions.

5. The parts of the catalyst surface from which the vaporization of positive ions takes place may be considered active or volcanic centers.

Recent work done by Barton and Harnwell at Princeton, through the courtesy of Prof. K. T. Compton, on the mass spectrograph of the positive ions emitted will give further information as to the nature of these ions. The probable significance of positive ion emission in surface catalysis will be discussed in a later paper.

In conclusion, the writer wishes to acknowledge suggestions given and the interest shown in these studies by Dr. S. Karrer and other members of the Laboratory staff, and especially the careful work of Mr. R. A. Nelson in the construction of the apparatus and his assistance in the experimental work.

Fixed Nitrogen Research Laboratory,
U. S. Department of Agriculture,
Washington, D. C.
December 12, 1925.

THE VISCOSITY OF AQUEOUS SOLUTIONS OF THE SILICATES OF SODA

BY V. R. MAIN

Introduction

Solutions obtained by dissolving fusions of soda ash and sand in water have an ever increasing application in industry, and are sold under the names "soluble glass" and "waterglass". The properties of such solutions are dependent on the proportions of the constituents used in the fusion, that most commonly met with being approximately of the composition 3.3 parts of silica to one part of soda. Very little is known with certainty regarding their chemical constitution. From commercial "waterglass", by addition of caustic soda and alcohol, Vesterberg[1] obtained crystals of the definite salt sodium metasilicate with 9, 6, and 3 molecules of water, from which he also obtained the anhydrous salt Na_2SiO_3. No crystalline salt containing a higher proportion of silica has been obtained.

A brief account of the viscosity of solutions of sodium silicate fusions is given in an article by W. Stericker[2] on "The Colloid Chemistry of Silica and its Derivatives", in which figures are given indicating the colloidal nature of the solutions. The slope of the viscosity-concentration curves is dependent on the ratio $Na_2O:SiO_2$ of the solution, being more abrupt the higher the proportion of silica. Stericker attributes the difference to one of two causes, or possibly to a combination of both: "a) Peptization of the colloidal material, and b) Formation of a crystalline compound at the expense of the colloidal constituents."

He points out the importance of the rate of change of viscosity from a technical standpoint, as a measure of the 'rate of set' when the solutions are used as adhesives. Stericker states that the viscosity-ratio curve passes through a minimum when the ratio $Na_2O:Sio_2$ is between 1:2 and 1:3 for a given concentration (% total solids) of the solution. No reference is made to the Journals in this article, and the work does not appear to have been published elsewhere. As the author gives no details of the method or apparatus used in determining the viscosity values, and does not state at what temperature they were made, the results may only be compared in a general way with those set forth in the present paper.

Materials

The present investigation was made with commercial samples of silicate of soda solutions provided by Brunner, Mond & Co. The analyses of these solutions are given in Table II. Traces of alumina and ferric oxide were found in the samples, insufficient, however, to affect appreciably the analysis figures.

---

[1] Proc. Eighth Int. Cong. Appl. Chem., **2**, 225 (1912).

[2] Bogue's "The Theory and Application of Colloidal Behavior," **2**, 563 (1924).

That these impurities exert a negligible influence on the viscosity measurements was satisfactorily demonstrated in the case of the solution of molar ratio $Na_2O:SiO_2 = 1:1$ where no difference in the viscosity was observed when a solution obtained by addition of caustic soda to a solution of higher ratio was compared with a solution of corresponding concentration prepared from crystals of sodium metasilicate free from impurity. The sample solutions provided vary in molecular ratio $Na_2O:SiO_2$ from 1:2 to 1:4.2. In addition to the solutions contained within this range, two others were investigated, one of ratio 1:1 and another of ratio ($Na_2O:SiO_2$) 2:1. These solutions were prepared by addition of the requisite amount of caustic soda to one of the solutions of higher silica content.

Method and Apparatus

The primary object of the present investigation was to discover whether viscosity measurements would throw any light on the nature of the silicates in solution, and for this purpose absolute measurements were not essential. It was therefore decided to measure viscosity relative to that of the solvent (water). All the silicate solutions, whatever the value of the ratio $Na_2O:SiO_2$ have at low concentrations a viscosity coefficient very little greater than that of pure water. In view of this fact, the method of efflux was chosen for the determination of viscosity, as the one most suited to the requirements. For this purpose two types of instrument are available:—

(a) The Oswald Viscometer, particularly suited to relative measurement, in which the liquid flows through the capillary under its own hydrostatic pressure. A certain volume of liquid is run into the instrument from a pipette, and flows from a small capacity bulb on one limb of a U-tube, to a large reservoir situated below the first bulb on the opposite limb of the tube, the time of flow between two marks, one above the small bulb and the other below it on the capillary itself, being measured for each solution. The same pipette is used giving the same volume flow in each case, and the pressure forcing the liquid through the capillary is thus directly proportional to the density of the liquid flowing. In the case of the more viscous solutions, sufficient time must be allowed for the liquid to drain from the pipette. The time of flow was measured at least five times for each solution, and each set of five readings was repeated with a fresh sample of solution. This method serves as a check on the introduction of error by variation in the volume delivered by the pipette. The values of the time of flow were generally in agreement to one-fifth second, an allowable error in the operation of the stop watch. The maximum error produced in the viscosity value on this account is 1%. The instrument was calibrated by measurement of the time of flow for distilled water, and this value was checked from time to time to ensure that the capillary was not affected by continued contact with the 'waterglass' solutions. The densities of the solutions were measured by means of a capillary pyknometer, by comparison of the weights of equal volumes of the solutions with the weight of the same volume of water at the temperature of the experiment. For the calculation of the relative viscosity, the viscosity and the density of water at 25°C are taken as unity.

The relative viscosity of a solution measured in this way is given by $\eta = k\rho t$

where ρ = density of the solution
and t = time of flow of the solution.

The value of k is the reciprocal of the time of flow for water. The instrument constants and the water values of the Ostwald instruments are tabulated below. Most of the measurements were made with the instrument A.

TABLE I

Instrument Constants

Viscometer	Length of Capillary	Volume of flow	Time of Flow for water	Value of k
	l(cms.)	V(cc.)	t_0(secs.)	$1/t_0$
A	12.95	4.32	25.9	.03861
A	12.95	4.32	26.2	.03816
B	11.10	2.82	80.0	.01250
C	9.65	3.28	37.1	.02695

The second value of t_0 for the instrument A was obtained by using a second pipette delivering a slightly larger volume of liquid. Most of the results were obtained using this pipette.

(b) The Variable Pressure Type of Viscometer, developed by Ubbelohde, in which the liquid is forced through the capillary under an applied pressure of gas. This instrument has the advantages that the time of flow in the case of the more viscous solutions may be conveniently reduced and the density of the solution need not be accurately known. The two bulbs are of the same volume and shape and are placed one on each limb of the U-tube and at the same height. The apparatus is arranged as shown in Fig. 1.

The nitrogen cylinder A used to obtain the necessary pressure is connected with a large pressure reservoir B, from which a T-piece allows connection with a water-manometer C, and with the viscometer D, through a three-way tap E. The latter enables the viscometer to be connected with the rest of the apparatus, or to be opened to the air. The pressure is adjusted and the time required for the liquid meniscus to pass the constrictions x and y is measured. To facilitate the readings, the constrictions are marked. The viscometer, situated inside a thermostat, is constructed with the bulbs in the form of double cones, to facilitate the drainage of the more viscous solutions, and the entrances to the capillary are slightly trumpet-shaped for the same reason. The constrictions (x and y) must not be too narrow, or a film of liquid forms across them which sets up a back pressure during the flow of liquid through the instrument.

A large aspirating bottle was the most suitable thing available as a pressure reservoir, and it was found that the manometer level fell through several millimetres during the flow. This fall is, however, accounted for by the change in gas volume in the apparatus due to the displacement of the liquid in the viscometer. The mean of manometer readings immediately before and after the observed flow is taken as the average pressure causing the flow. This is not necessarily the true average pressure, but corrections due to the density of the solution when the bulbs in the viscometer are not at the same height, and the corrections for outside effects, are small, and as absolute measurements were not required, are not applied[1].

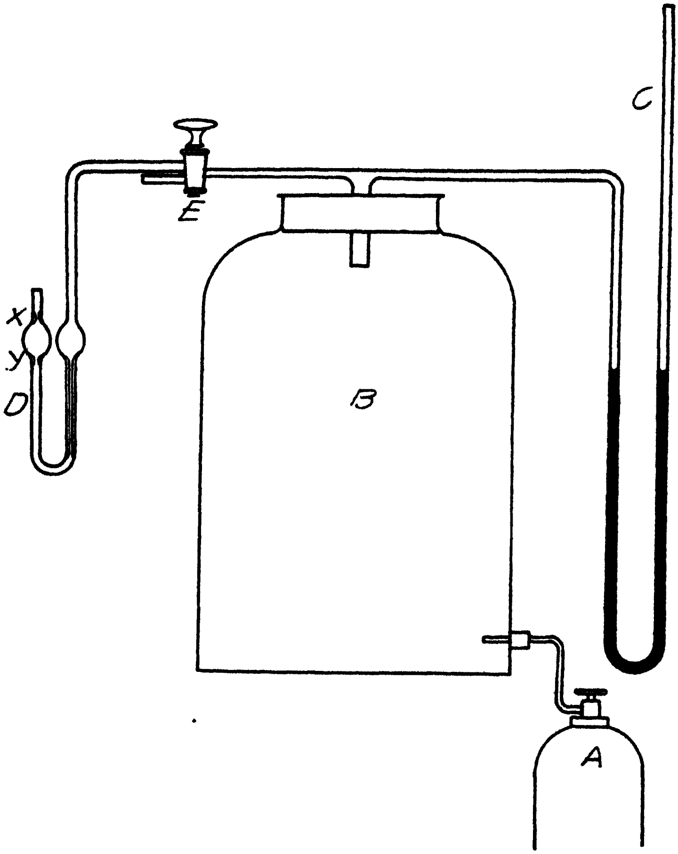


FIG. 1

The method originally employed by experimenters using this type of instrument consisted in measuring the time of flow for each solution, at the same constant pressure. The viscosity of liquids, however, and more especially that of colloidal solutions, has been shown to be dependent on the rate of shear in the viscometer, and hence on the rate of flow, the volume flowing being constant[1].

---

[1] For these corrections see Bingham: "Fluidity and Plasticity," 298 (1922); Kendall and Monroe: J. Am. Chem. Soc., 39, 1787 (1917).

It therefore seemed more satisfactory to compare the pressures required to cause all solutions to flow through the capillary at the same rate of flow, when the conditions in the capillary would be more nearly the same regarding shearing force, though the actual shearing which occurs in the solution is dependent on the latter. This method offers considerable experimental difficulty, the pressure requiring very fine adjustment. In the present investigation a series of values was obtained for each solution, the time of flow being measured for a large number of pressure values. An example of such a series is given in Table XIV.

The equation of Poiseuille with the later correction for the kinetic energy as the liquid leaves the capillary may be applied to these results, namely

$$\eta = \frac{\pi g p r^4 t}{8 v l} - \frac{m \rho V}{8 \pi l t}$$

where p = pressure producing flow
t = time of flow
r = radius of capillary
l = length of capillary
V = volume of liquid flowing
ρ = density of solution
and m = a determined constant.

The equation may be written:—

$$\eta = Cpt - C'\rho/t$$

The values of C and C′ are then given by

$$C' = \frac{mV}{8\pi l} \quad \text{and} \quad C = \frac{\eta_o t_o + C'\rho_o}{p_o t_o^2}$$

where the suffix o indicates measurements made for distilled water. The above method of calculating C, obviates the necessity of measuring the radius of the capillary (r), error in which is greatly increased in the value of C obtained directly, since C is proportional to the fourth power of the radius. The application of this formula is further discussed with particular reference to the results obtained at a later stage.

Experimental

All determinations were made at a temperature of 25°C. in an air-thermostat provided with a glass door. The temperature was controlled by means of an electrical relay system, and was constant during a determination to 1/10°C. The thermometer was carefully checked by comparison with an accurate standard. Before use, viscometers were washed with caustic soda, chromic acid mixture, and distilled water, and were subsequently dried in an electric oven.

---

[1] Hatschek: Kolloid-Z., **8**, 34 (1911); **13**, 88 (1913); Garret: Diss. Heidelberg, (1903); Phil. Mag., **6**, 374 (1903).

Solutions of different concentrations of each ratio were prepared by dilution of the sample, and concentration values are calculated in weight normality with respect to the sodium oxide content. After preparing a solution in this way, it is well shaken and is allowed to stand overnight. This precaution was taken to ensure a thorough mixing of the silicate solution with the water added. There is a tendency for the water to remain as a separate layer in the case of dilution of the more viscous samples. Mixing could be obtained by vigorous agitation of the containing vessel, but this caused a large number of small air bubbles to form in the solution which rise to the surface only very slowly.

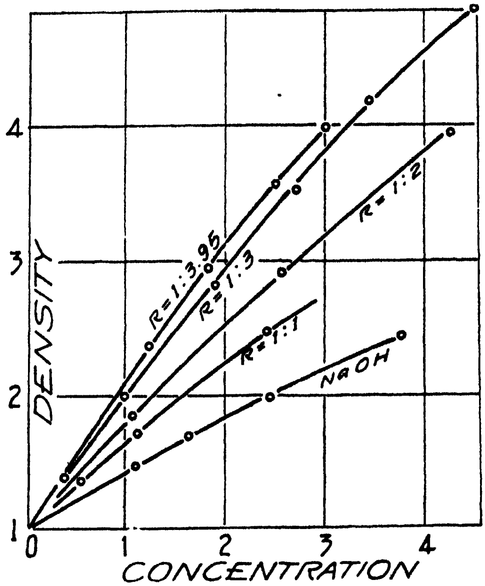


FIG. 2

Values were also obtained in the Ostwald viscometer for caustic soda solutions for purposes of comparison. No change in the viscosity of the solutions, which have been prepared as described, was observed over a period of several weeks.

TABLE II

Analysis of the Solutions

Molecular Ratio $Na_2O:SiO_2$	Percentage Analysis of Sample Na_2O	SiO_2	H_2O
1 : 2.0	18.50	36.00	45.50
1 : 2.5	13.80	32.90	53.30
1 : 3.0	9.06	26.44	64.50
1 : 3.3	9.50	30.50	60.00
1 : 3.8	7.16	26.26	66.58
1 : 3.95	6.45	24.88	68.67
1 : 4.2	5.29	21.51	73.20

The Relative Density

The relative density of solutions at 25°C. was determined by means of a pyknometer, the volume of liquid in the instrument being each time adjusted to a mark etched on the capillary. Duplicate determinations were in agreement to within .01%.

The density-concentration curves exhibit slight concavity to the concentration axis. Examples of these are given in Fig. 2, the curves here reproduced being those for caustic soda solutions, and silicate solutions of ratios (Na_2O: SiO_2) 1:1, 1:2, 1:3 and 1:3.95. The values of density from which these curves are drawn are tabulated with the viscosity results in Tables IV to XIII.

From density-concentration curves, values are obtained by interpolation for the ratios investigated at the definite concentrations $1N_w$, $2N_w$ and $3N_w$, the symbol N_w representing weight normality of soda, or the number of gram *equivalents* of Na_2O contained in 1000 gms. of water. These results appear in Table III and are represented graphically in Fig. 3.

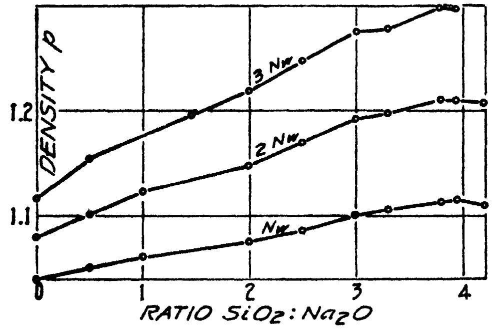


Fig. 3

The curves in this diagram represent the effect of addition of silica on the density of caustic soda solutions, the values on the density axis being those obtained for pure caustic soda solution.

Table III

Density-Ratio SiO_2:Na_2O

Molecular Ratio. SiO_2:Na_2O	Conc. N_w	Density ρ	Conc. N_w	Density ρ	Conc. N_w	Density ρ
NaOH	1.0	1.040	2.0	1.080	3.0	1.116
1 : 2	"	1.052	"	1.101	"	1.150
1 : 1	"	1.062	"	1.123	"	——
2 : 1	"	1.075	"	1.147	"	1.217
2.5 : 1	"	1.085	"	1.168	"	1.247
3.0 : 1	"	1.099	"	1.190	"	1.274
3.3 : 1	"	1.105	"	1.195	"	1.276
3.8 : 1	"	1.111	"	1.208	"	1.296
3.95 : 1	"	1.113	"	1.207	"	1.295
4.2 : 1	"	1.109	"	1.205	"	——

With increasing content of silica the solutions exhibit a gradual rise in density until the ratio 1:4 ($Na_2O:SiO_2$) is approached, when the density shows no further rise, but in fact falls slightly when the proportion of silica is further increased. The maximum density value occurs in each case in the neighborhood of the ratio 1:4, but in the more concentrated solutions the maximum occurs at a value of the ratio where the silica content is slightly lower than that represented by this value.

No very certain interpretation can be given of this maximum, but it is known, and viscosity measurements show, that the solutions richer in silica are more colloidal in properties than those in which the proportion of silica is less, and that the colloidal properties are exhibited at lowers values of the ratio SiO_2/Na_2O when the concentration is high. It seems possible therefore that the effect on the density may be due to a change in the hydration of the colloidal constituent.

Relative Viscosity

Results obtained with Ostwald Instruments

TABLE IV

Viscosity of Caustic Soda

Viscometer No.	Concentration N_w	Time t(secs.)	Density ρ	Viscosity η
A.	3.782	50.9	1.1423	2.219
B.	2.469	121.0	1.0959	1.658
A.	1.657	34.2	1.0687	1.395
B.	1.114	95.6	1.0464	1.250

TABLE V

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 2:1

Viscometer No.	Concentration N_w	Time t(secs.)	Density ρ	Viscosity η
A.	6.033	139.5	1.2821	6.879
A.	2.801	49.6	1.1411	2.177
A.	2.130	41.2	1.1103	1.759
A.	0.940	31.1	1.0506	1.257

TABLE VI

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 1:1

Viscometer No.	Concentration N_w	Time t	Density ρ	Visocsity η
A.	2.435	48.8	1.1458	2.158
A.	1.134	33.4	1.0705	1.381
A.	0.841	30.9	1.0529	1.256
A.	0.546	29.0	1.0352	1.159

TABLE VII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 1:2

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	6.277	569.0	1.4083	30.531
A.	4.274	154.1	1.2948	7.616
B.	4.274	487.4	1.2948	7.889
A.	2.586	65.3	1.1900	2.966
A.	1.088	36.1	1.0845	1.494

TABLE VIII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 1:2.5

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	6.114	1286.2	1.4450	71.483
A.	3.717	164.2	1.2938	8.171
A.	1.813	52.7	1.1543	2.340
A.	0.921	35.5	1.0815	1.477

TABLE IX

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 1:3

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	4.531	898.0	1.3868	47.532
A.	3.464	244.8	1.3177	12.312
A.	2.741	122.9	1.2507	5.867
A.	1.922	66.0	1.1816	2.977
A.	0.999	38.8	1.0994	1.628
A.	0.365	29.8	1.0379	1.180

TABLE X

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2$ = 1:3.3

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	5.108	3097.2	1.4231	1682
A.	3.785	529.0	1.3308	26.870
A.	2.758	145.6	1.2527	6.962
B.	1.851	207.2	1.1827	3.063
B.	1.157	133.0	1.1143	1.853
B.	0.542	98.8	1.0555	1.304

TABLE XI

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3.8$

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	3.469	3349.1	1.3353	170.69
B.	2.953	1583.3	1.2921	25.572
A.	2.953	496.1	1.2921	24.466
A.	2.543	217.6	1.2559	10.431
B.	2.061	348.4	1.2126	5.281
A.	1.044	43.8	1.1136	1.862

TABLE XII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:3.95$

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	3.030	2073.4	1.2989	103.582
C.	3.030	2970.4	1.2989	103.996
A.	2.530	307.0	1.2559	14.716
A.	1.852	96.6	1.1937	4.401
A.	1.247	52.1	1.1354	2.258

TABLE XIII

Viscosity of Silicate Solution. Ratio $Na_2O:SiO_2 = 1:4.2$

Viscometer No.	Concentration N_w	Time t	Density ρ	Viscosity η
A.	2.331	323.8	1.2362	15.395
A.	1.977	140.2	1.2044	6.494
A.	1.496	70.0	1.1589	3.120
A.	0.982	44.0	1.1075	1.874
A.	0.474	32.2	1.0541	1.305

These data are plotted in Fig. 8 and are considered in detail after presentation of the further results.

Results obtained with Ubbelohde Instruments

A complete series of measurements of time of flow over a range of different values of pressure is given in Table XIV, and the remainder of the results are condensed into Tables XV to XXII, and are graphically represented in Figs. 4, 5, and 6, where values of the logarithm (of the applied pressure) are plotted as ordinates and the negative logarithm of the reciprocal of the time of flow as abscissae, the value of 1/t being proportional to the velocity of flow. These figures contain data chosen from a range of experimental values. The extreme values are presented in each case, and a convenient number of inter-

TABLE XIV

Values obtained for 2.586 N_W Solution. Ratio $Na_2O:SiO_2$ = 1:2 in Viscometer U 2.

Manometer Readings.		Pressure p(cms.)		Time t(secs.)	Log p	Log 1/t	Log α
53.44	6.08	47.36	46.86	98 1/5	1.6708	1.9786	3.654
52.94	6.59	46.35					
52.50	7.09	45.41	44.91	99.1	1.6524	1.9961	3.654
52.00	7.60	44.40					
51.42	8.22	43.20	42.65	104 2/5	1.6289	2.0187	3.653
50.90	8.80	42.10					
50.01	9.70	40.31	39.80	111.3	1.5999	2.0465	3.651
49.51	10.22	39.29					
49.44	10.30	39.14	38.64	114 4/5	1.5870	2.0599	3.652
48.95	10.81	38.14					
48.37	11.43	36.94	36.38	121.9	1.5609	2.0859	3.652
47.81	11.99	35.82					
46.88	12.98	33.90	33.42	132 1/5	1.5240	2.1212	3.650
46.41	13.47	32.94					
46.41	13.46	32.95	32.30	136	1.5119	2.1335	3.650
45.96	13.91	32.05					
45.66	14.21	31.45	30.91	143	1.4901	2.1553	3.650
45.13	14.77	30.36					
44.38	15.57	28.81	28.32	155 3/5	1.4521	2.1920	3.649
43.89	16.07	27.82					
43.34	16.64	26.70	26.23	167.9	1.4188	2.2251	3.645
42.87	17.12	25.75					
42.42	17.59	24.83	24.38	180 3/5	1.3870	2.2567	3.648
41.99	18.06	23.93					
41.51	18.53	22.98	22.51	195.7	1.3524	2.2916	3.648
41.04	19.01	22.03					
40.35	19.76	20.59	19.95	220 2/5	1.3000	2.3432	3.647
39.71	20.40	19.31					
39.17	20.98	18.19	17.77	246 3/5	1.2497	2.3920	3.646
38.75	21.40	17.35					
38.07	22.11	15.96	15.37	278	1.1867	2.4440	3.634
37.49	22.72	14.77					
37.10	23.06	14.04	13.52	324.7	1.1310	2.5115	3.646
36.58	23.59	12.99					
35.89	24.32	11.57	11.04	399	1.0429	2.6010	3.647
35.36	24.85	10.51					
35.41	24.80	10.61	10.04	443 4/5	1.0017	2.6472	3.652
34.86	25.39	9.47					
34.76	25.50	9.26	8.53	525.9	0.9310	2.7209	3.655
34.04	26.24	7.80					

mediate points are inserted. All the intermediate values measured are not reproduced because they give rise to a large number of points lying close together on the figures, but the values not included lie equally well upon the curves.

The relation between the time of flow and the applied pressure producing the flow may be expressed by the equation

$$\text{Log } 1/t = n \log p - \log \alpha$$

where n and α are constants and are obtained graphically. The numerical value of Log α is given by the intercept on the Log 1/t axis, and the value of *n* by the slope of the straight line to the Log p axis.

The relation between the time of flow *t*, and the pressure *p*, producing the flow, may be written

$$p^n t = \alpha$$

the Poiseuille equation representing linear or viscous flow is of the form pt = constant, and is thus a special case of a general equation, characterised by the condition n = 1. If the value of *n* is not unity, the conditions of flow do not satisfy Poiseuille's Law and the function measured by $Cp^n t$ where C is an apparatus constant, is not a true viscosity coefficient.

The values contained in the last column of Table XIV are calculated for each result, using the value of *n* obtained graphically, and serve to show the agreement with the above law. The greatest deviation in the value of Log α neglecting the value 3.634 which is obviously due to an error in manipulation, is less than 0.3%.

TABLE XV

Ratio $Na_2O:SiO_2$ = 1:1

No. of curve.	Viscometer No.	Concentration N_w	Logα	n	α/α_0
a.	U.2.	2.435	3.496	0.986	2.649
b.	U.2.	1.133	3.272	0.981	1.581
c.	U.2.	0.702	3.200	0.960	1.340
d.	U.2.	0.505	3.166	0.960	1.239
e.	U.2.	0.202	3.136	0.960	1.156

TABLE XVI

Ratio $Na_2O:SiO_2$ = 1:2

No. of curve	Viscometer No.	Concentration N_w	Logα	n	α/α_0
E.	U.2.	6.277	4.677	0.996	40.179
A.	U.3.	6.277	3.177	1.001	28.840
B.	U.3.	4.274	2.631	1.020	8.204
C.	U.2.	2.586	3.657	1.003	3.837
D.	U.2.	1.088	3.370	1.011	1.982

TABLE XVII

Ratio $Na_2O:SiO_2$ = 1:2.5

No. of curve	Viscometer No.	Concentration N_w	Log α	n	α/α_0
f.	U.6.	3.717	3.436	1.000	8.531
g.	U.6.	1.813	2.862	0.953	2.275
h.	U.6.	0.921	2.618	0.907	1.297

TABLE XVIII

Ratio $Na_2O:SiO_2$ = 1:3

No. of curve	Viscometer No.	Concentration N_w	Log α	n	α/α_0
n.	U.4.	4.531	3.840	1.032	62.373
o.	U.4.	3.464	3.210	1.008	14.622
p.	U.4.	2.741	2.903	1.006	7.211
q.	U.4.	1.922	2.553	0.954	3.221
r.	U.4.	0.999	2.260	0.912	1.641
s.	U.4.	0.365	2.125	0.887	1.202

TABLE XIX

Ratio $Na_2O:SiO_2$ = 1:3.3

No. of curve	Viscometer No.	Concentration N_w	Log α	n	α/α_0
F.	U.2.	3.785	4.560	0.963	30.690
G.	U.2.	2.758	4.051	1.024	9.506
H.	U.2.	1.851	3.629	0.986	3.598
I.	U.2.	1.157	3.437	1.001	2.312

TABLE XX

Ratio $Na_2O:SiO_2$ = 1:3.8

No. of curve	Viscometer No.	Concentration N_w	Log α	n	α/α_0
i.	U.5.	2.953	3.482	1.013	35.237
k.	U.5.	2.543	3.108	1.009	14.894
l.	U.5.	2.061	2.778	0.993	6.966
m.	U.5.	1.044	2.408	1.034	2.972

TABLE XXI

Ratio $Na_2O:SiO_2$ = 1:3.95

No. of curve	Viscometer No.	Concentration N_w	Log α	n	α/α_0
t.	U.5.	3.030	3.900	0.882	92.257
t.	U.1.	3.030	3.810	1.004	117.22
u.	U.5.	2.560	3.250	1.004	16.406
v.	U.5.	1.852	2.730	1.001	6.237
w.	U.5.	1.247	2.387	0.950	2.831
x.	U.1.	2.862	3.355	0.977	41.115

TABLE XXII

Ratio $Na_2O:SiO_2 = 1:4.2$

No. of curve	Viscometer No.	Concentration N_w	Logα	n	α/α_0
J.	U.6.	2.331	3.734	1.010	16.943
K.	U.6.	1.977	3.354	1.010	7.063
L.	U.6.	1.496	2.989	0.956	3.048
M.	U.6.	0.982	2.751	0.938	1.762
N.	U.6.	0.474	2.600	0.920	1.245

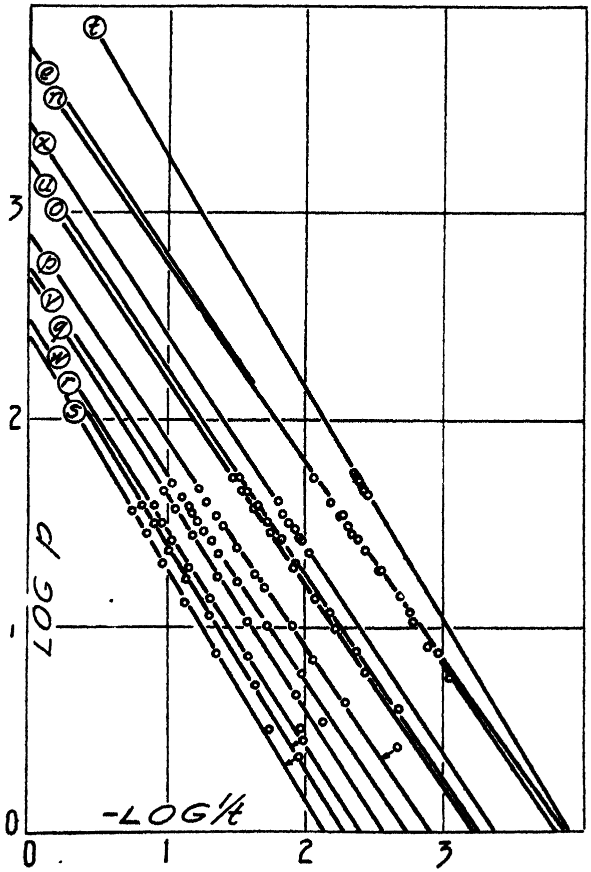


FIG. 4

The values of Log α_0 from which the ratio α/α_0 given in the last column of Tables XI to XXII is calculated, are the values of the intercept on the Log 1/t axis of the straight line[1] representing the flow of water through the viscometer, and are obtained as calibration constants for each instrument.

---

[1] Obtained when − log 1/t is plotted against log p.

It will be seen from Figs. 4, 5, and 6, that for the more dilute solutions the extreme points lie somewhat off the straight line, and it is not certain that the straight line is here a true representation of the law of flow of the liquid. It should, however, be noted that the divergences are small and occur where (a) the pressure is very small and (b) with small values of time of flow; in both of these cases the experimental errors (a) in reading the manometer, and (b) in operation of the stop-watch, are greater than for values intermediate between the extremes. Also the divergence is only observed in the less viscous solutions with relatively small times of flow, when the effect of the kinetic energy correction (not applied in these results) is a maximum. It therefore seems justifiable to state that under the conditions of pressure employed the flow obeys the law expressed by the equation

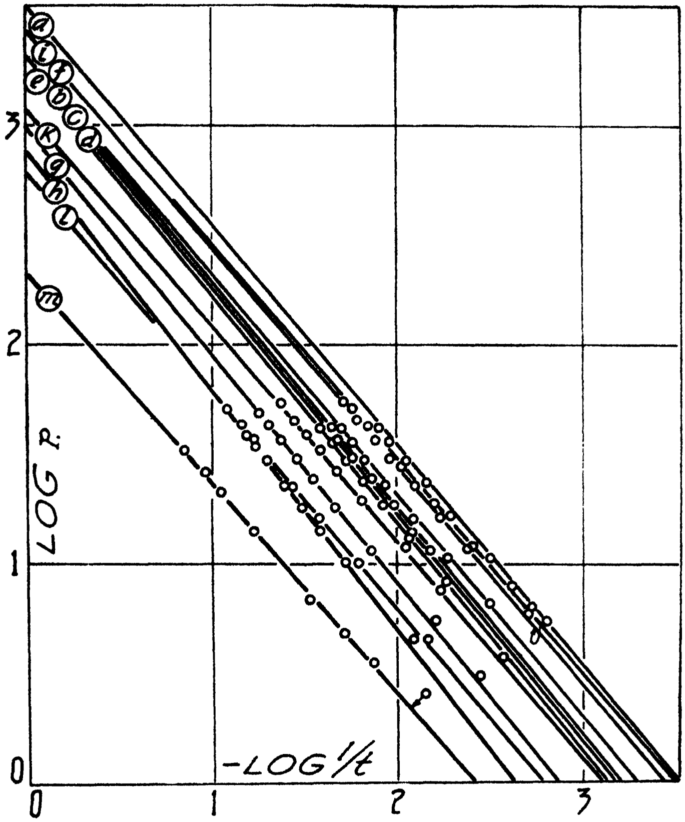


FIG. 5

Farrow[1], working on starch pastes, found that using the equation

$$V/t = kP^n$$

where V is the volume flowing in the t under a pressure P, the value of N was independent of the instrument used, but changed from paste to paste and increased with increasing concentration, being always greater than unity. It is claimed that the value of N is an important property of the starch paste, as much so in fact as the value of the 'coefficient of flow', a term used in place of viscosity on account of the fact that N is not unity. The value of this coefficient was found to be dependent on the instrument used.

---

[1] J. Textile Inst., 14, 11 (1923).

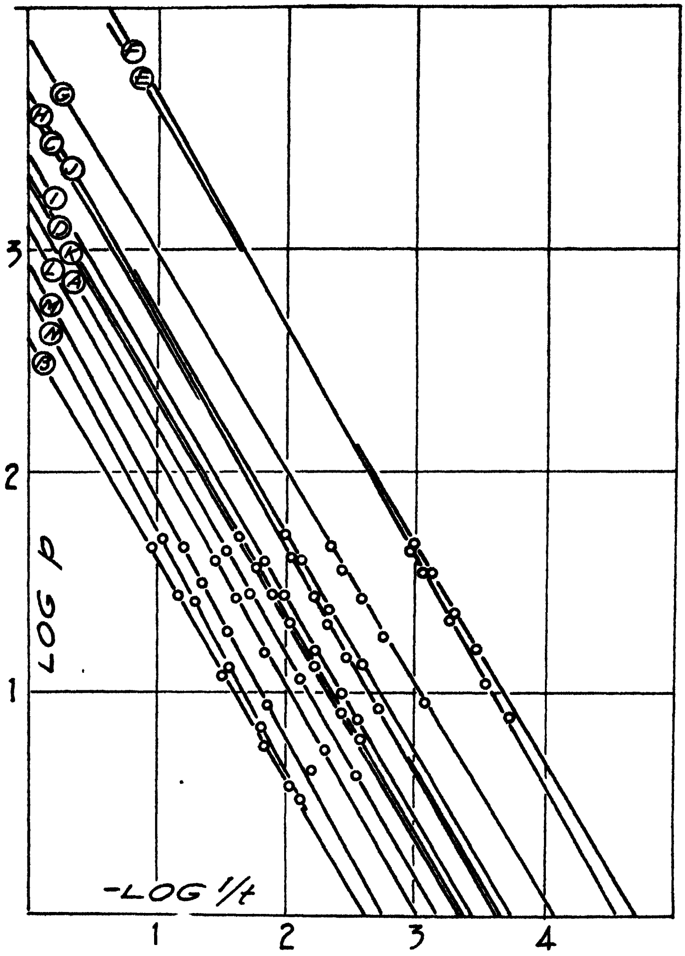


Fig. 6

The value of the exponent n in the present investigation bears no relation to the nature of the solution examined, as in the case of the starch pastes. In fact, in the case of the ratio 1:1, the value of n remains 0.960 though the concentration is increased from 0.2 to 0.7 N_w. In Table XX also, the value of n remains almost constant though the concentration is almost trebled. Similarly, with increasing proportion of silica in the solutions, the value of n does not change in any regular way, but shows only a divergence from a mean value. The value of the exponent is also independent of the instrument used, showing a deviation from a mean value of about 2%. The same order of agreement in the value of n is observed in the cases of changing concentration or of proportion of silica in the solution. The mean value of n over the whole range is 0.979 which is very close to the condition $n = 1$ for viscous flow obeying Poiseuille's Law.

The exponent thus shows little variation with change of instrument and is unaffected by the varying composition of the solutions, being in general very nearly unity.

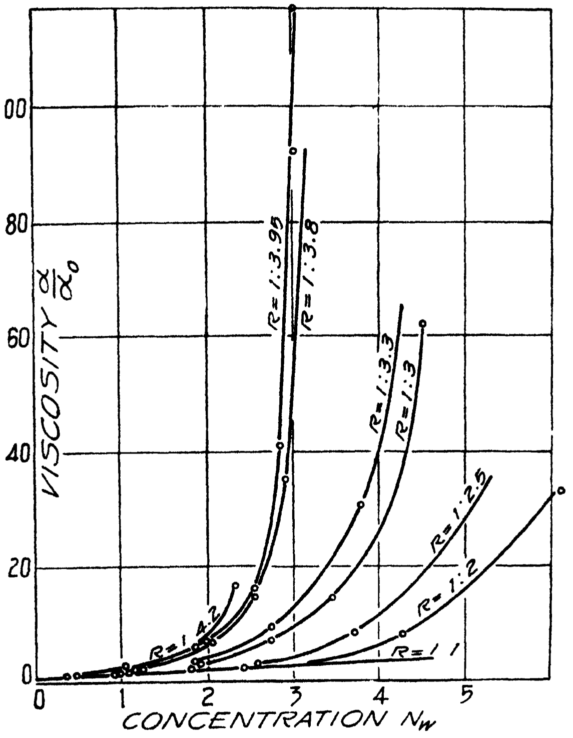


FIG. 7
Results with Ubbelohde Viscometers

The value of α obtained from the intercept on the negative Log 1/t axis is used as a measure of the viscosity. The equation expressing the viscosity of solutions measured in this type of instrument will now become

$$\eta = Cp^n t - C'p/t,$$

the second term being a correction for kinetic energy. The coefficient η is not strictly a true viscosity coefficient, since the conditions are not those required by the Law of Poiseuille, but it is used as such in the expression of these results since n is not greatly different from unity.

The corrective term is in general small compared with the first term, and the error introduced by neglecting the correction is not more than 2 or 3%, an error of the same order as that incurred in the determination of the constants n and α of the straight lines representing the flow. Moreover, the difference between values obtained for the same solution in two different instruments, irrespective of whether any correction is applied or not, is far greater than the correction to be applied. In view of these considerations it seemed superfluous to correct the values obtained in these instruments for kinetic energy at the capillary exit.

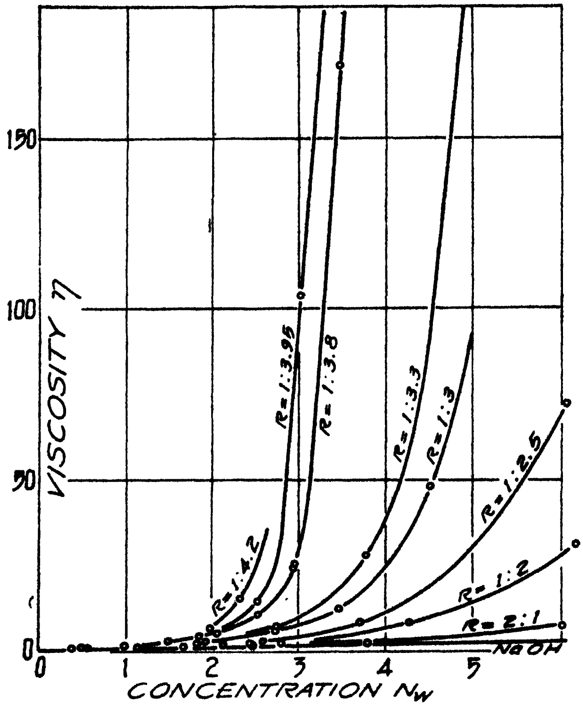


Fig. 8
Results with Ostwald Viscometer

The value of the viscosity coefficient relative to that of water at the same temperature, neglecting the kinetic energy correction, becomes:

$$\eta = \frac{p^n t}{p_0^{n_0} t_0},$$

where the values in the numerator are for the solution and those in the denominator for water. This ratio may be expressed as α/α_0 and the values of viscosity expressed in this way (α and α_0 being obtained graphically in the manner already described) are given in the last column of Tables XV to XXII.

The values of α/α_0 taken as a measure of relative viscosity are represented in Fig. 7, each curve indicating the change of the function with increasing concentration for a solution of fixed ratio $Na_2O:SiO_2$. The concentration is expressed in weight normality with respect to the Na_2O content of the solution, for reasons discussed later. Fig. 8 gives the results of determinations of relative viscosity made in the Ostwald type of instrument, the data from which these curves are drawn appearing in Tables IV and XIII. The two figures show certain differences apart from the fact that the values of α/α_0 (Fig. 7) lie, in general, above those of η (Fig. 8) for the same value on the concentration axis, the difference varying with the instruments used, and with the viscosity of the solution investigated, the maximum differences being 20-25%. Thus, in the case of the measurements made with the Ostwald instrument, the curves showing the behavior of solutions of high silica content lie comparatively above those where the silica content is lower. The values of α/α_0, however, do not exhibit this characteristic at low concentrations. Here, however, different viscometers were used in the determinations of α and it has already been pointed out that the value of α/α_0 is dependent on the instrument used. This is sufficient to account for the discrepancy here observed, the difference between the values obtained in different instruments being in all probability due mainly to the different average rate of shear in the capillaries.

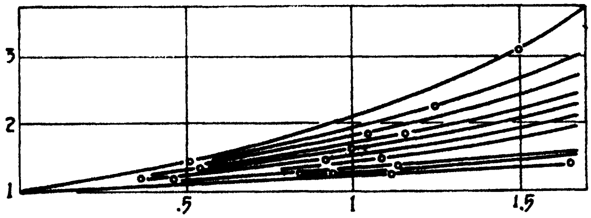


FIG. 8a

The curves of both figures, however, show the same general characteristics, and are typical of emulsoid or lyophile systems, where increase in concentration at low concentrations produces only a small increase in viscosity until a certain concentration is reached, when there is a very rapid rise in viscosity, and the latter is increased enormously by very small increase in concentration. The point at which this rapid increase in the slope occurs is dependent on the composition of the solution with regard to silica content. The ratios of high soda content show only a very gradual change of slope, and as the proportion of silica is increased the change of slope becomes more rapid until as the ratio 1:4 is approached, the curve rises very steeply and with small increases in concentration becomes almost vertical. Measurements made under these conditions become somewhat uncertain because very small changes in concentration exert an enormous influence on the viscosity, and the solutions at such concentrations evaporate very readily when exposed to the air, and consequently must be introduced into the instrument as rapidly as possible. Rapid transference from the containing bottle to the viscometer is difficult on account of the slow drainage from a pipette. The significance of the almost vertical portions of the curves would seem to indicate an approach to the gel state. In this connection work, as yet unpublished, on the preparation of silicate solutions by electrolytic methods carried out by R. W. Harman in this laboratory, may be mentioned, when a solution of low concentration and ratio approximately 1:5 was found to form a gel on standing for a few days.

At low concentrations the curves approach one another very rapidly. The lower portion of the curves of Fig. 8 are reproduced in Fig. 8a on a much larger scale, when they are still graded according to silica content, approaching the viscosity axis together at zero concentration, a value representing the viscosity of water.

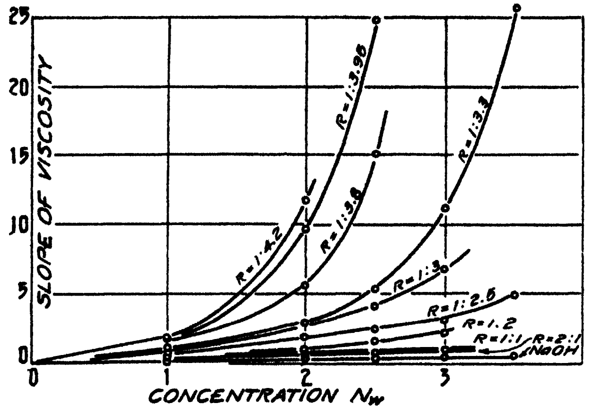


FIG. 9

The value of concentration at which the slope of the viscosity-concentration curve begins to change rapidly is much lower in the case of solutions containing a high proportion of silica than in those where the silica content is lower. This is well shown in Fig. 9, where the slope of viscosity is plotted against concentration. The slope rises in a normal manner until the concentration $1 N_w$ is reached, when it begins to change more or less rapidly depending on the ratio $Na_2O:SiO_2$ of the solution. With ratio 1:4.2 at the concentration 1.5 N_w the slope of the viscosity-concentration curve is 5, while with the ratio 1:2.5 a concentration of 3.5 N_w is required to give the same slope, and a concentration of 2.5 N_w for the ratio 1:3.3. There seems to be a very rapid increase in colloidal properties between the ratios 1:3.3 and 1:3.8, the curves for the latter being considerably higher than the ratios of lower silica content. With the solutions of ratio 1:1 and 2:1 the change of slope with increasing concentration is almost linear up to the highest concentrations investigated, and comparable with the curve for caustic soda solutions, though the actual values of the slope at given concentrations are higher. From this fact it is concluded that there is very little, if any, colloidal material present in the solutions until the ratio $Na_2O:SiO_2$ reaches the value 1:2.

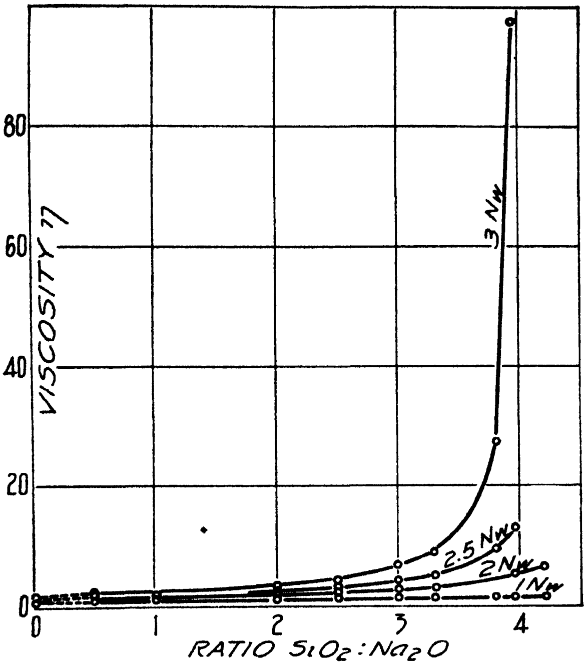


FIG. 10
Ostwald Viscometer

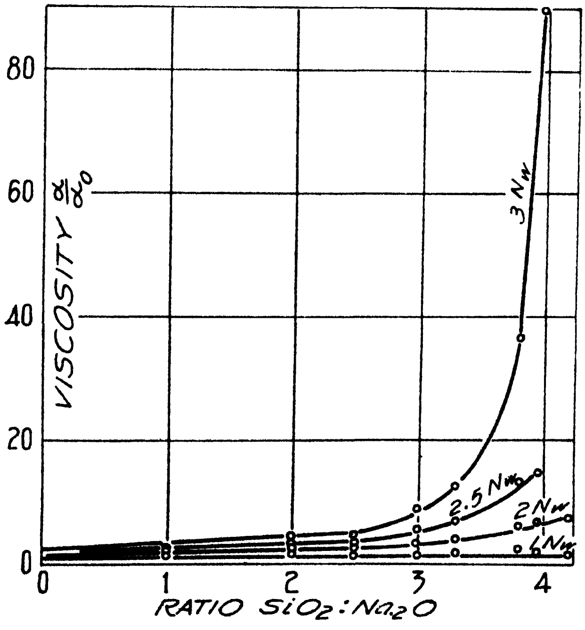


FIG. 11
Ubbelohde Viscometers

The Effect of the Ratio $Na_2O : SiO_2$ on the Viscosity

From the curves representing the relation between viscosity and concentration, values are obtained by interpolation, of the viscosity of the solutions at each ratio $Na_2O:SiO_2$ investigated, at concentrations (N_w, $2N_w$, $2.5N_w$ and $3N_w$. The values so obtained are plotted as ordinates against the ratio SiO_2/Na_2O as abscissae. The results are tabulated in Table XXIII and are graphically represented in Fig. 10. These curves show the influence of increasing silica content on the viscosity of solutions up to the ratio $Na_2O:SiO_2 = 1:4.2$. The values on the viscosity axis are those for pure caustic soda solutions.

TABLE XXIII.

ratio $SiO_2:Na_2O$	Conc. N_w	Viscosity		Conc. N_w	Viscosity		Conc.	Viscosity		Conc.	Viscosity	
		η	α/α_0		η	α/α_0		η	α/α_0		η	α/α_0
Caustic soda	3.0	1.86	—	2.5	1.67	—	2.0	1.50	—	1.0	1.22	—
1:2.0	"	2.34	—	"	1.93	—	"	1.70	—	"	1.28	—
1.0	"	—	—	"	2.21	2.73	"	1.86	2.24	"	1.31	1.49
2.0	"	3.79	4.69	"	2.81	3.68	"	2.18	2.90	"	1.42	1.79
2.5	"	4.70	5.05	"	3.43	3.63	"	2.50	2.70	"	1.49	1.50
3.0	"	7.32	9.18	"	4.60	5.90	"	3.19	3.58	"	1.61	1.62
3.3	"	9.38	12.95	"	5.42	7.23	"	3.48	4.37	"	1.68	2.05
3.8	"	27.65	37	"	9.79	13.83	"	4.87	6.50	"	1.79	2.78
3.95	"	98	90	"	13.40	15.00	"	5.49	7.10	"	1.90	2.30
4.2	"	—	—	"	—	—	"	6.77	7.75	"	1.87	1.80

The values of α/α_0 taken as a measure of relative viscosity are plotted in Fig. 11, and give a curve of the same general type as that of Fig. 10 obtained by using the Ostwald type of Viscometer. If, however, the two curves are plotted on a larger scale as is done in Fig. 12, the values of the relative viscosity obtained in the Ostwald instruments still lie on smooth curves, but the values obtained in the pressure-type of instrument, while of the same general nature, though higher throughout, exhibit the minimum obvious from the above table between the ratios ($Na_2O:SiO_2$) 1:2 and 1:3.

It is between these two ratios that Stericker (loc. cit.) observed a minimum in viscosity, and in fact the dotted curves of Fig. 12 bear a very strong resemblance in form to his curves. Unfortunately, no significance can be attached to this minimum, which does not appear when the Ostwald viscometer is used, all measurements being made in the same instrument. The minimum may be due solely to the use of a number of instruments in determining the flow, and have no connection with the nature of the solutions themselves. In the higher concentrations the minimum disappears, as the values for the concentration $3N_w$ (Table XXIII) indicate, which supports the view that it is due to the effect of unknown factors influencing the flow, the velocity of flow being much smaller at these higher concentrations in all the instruments used.

In considering the effect of ratio on the viscosity of the solutions, the reason for expressing concentration with respect to Na_2O content becomes evident. If the concentration is expressed as total percentage of solids present, which at first sight seems the most reasonable mode of expression for viscosity measurements, and the values of viscosity at given concentrations are plotted against the ratio SiO_2/Na_2O, the curves obtained are irregular and very difficult to interpret. This is because the content of the solutions of different ratio is changing with respect both to soda and to silica. Thus a 30% solution of ratio $Na_2O:SiO_2 = 1:2$ contains 19.82 gms. SiO_2 and 10.18 gms. Na_2O, while a solution of composition $Na_2O:SiO_2 = 1:3.8$ of the same percentage content contains 23.57 gms. SiO_2 and 6.34 gms. Na_2O per 100 gms. of solution.

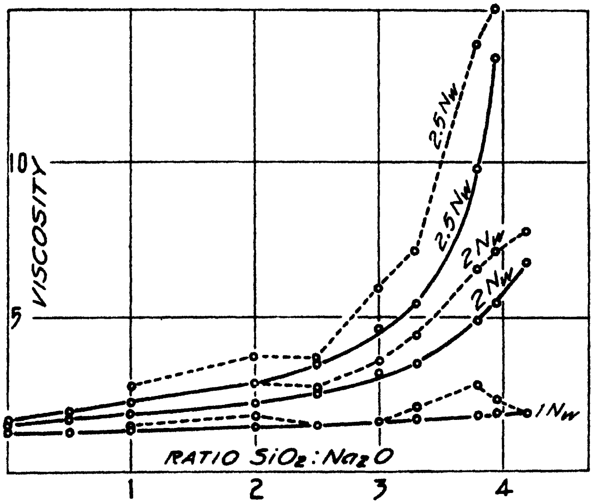


FIG. 12

If, however, as is done here, the concentration is expressed in normality with respect to one constituent, the concentration of that constituent remains constant as the ratio is increased. The equivalent content of soda is chosen rather than that of SiO_2 because solutions of corresponding Na_2O content containing no silica may be used for viscosity measurement, and the values inserted in the curves which represent the effect on viscosity of addition of silica to a solution of caustic soda, the weight of Na_2O per 100 gms. of water being constant throughout, for each curve considered separately.

At low concentrations the change of viscosity with increasing proportion of silica is not very great, and for concentrations up to $1N_w$ the viscosity-ratio curve is almost linear. At higher concentrations the viscosity is, of course, higher throughout, and the points lie on smooth curves exhibiting marked change of slope, as the proportion of silica is increased. When the concentration is $2N_w$ the slope changes gradually until the ratio 1:4 is approached, when a large increase in viscosity occurs with small increase in silica content. As the concentration is still further increased, the value of the ratio at which the slope of the curve begins to increase sharply is less. Thus at $3N_w$ the curve bends up sharply at the ratio 1:3 (Na_2O:SiO_2). At all concentrations investigated no very rapid change of slope occurs in the viscosity-ratio curves until the ratio 1:2 is reached. Above this value the slope begins to increase more rapidly, the actual value of the ratio at which the change is most marked being dependent on the concentration of the solution. The higher the concentration the lower will be the value of the ratio at which this change is observed. The curve for the concentration $3N_w$ rises almost vertically as the ratio approaches 1:4, and it is doubtful whether a solution of such concentration could be prepared containing a higher proportion of silica and still have the properties of a fluid.

Conclusions

These curves undoubtedly indicate a change in the colloidal nature of the solution as the proportion of silica is increased. Below the ratio Na_2O:SiO_2 = 1:1 the viscosity increase is normal, and at low concentrations at any rate the solutions are probably entirely crystalloidal, in which case they may be considered as solutions either of a series of definite salts or as a mixture of the known salt sodium metasilicate in solution with free caustic soda. Between the ratios 1:1 and 1:2 where the viscosity-ratio curve still shows little evidence of colloidal material, a salt of the composition Na_2SiO_3 may be present or the solution may be considered as containing the metasilicate together with non-colloidal silica acid. No definite conclusion as to the existence of definite salts in solution can be drawn from the measurement of viscosity alone, but it can be generally inferred that below the ratio 1:2 very little or no colloidal material is present in the solution under the conditions of concentration investigated.

While no very definite conclusion as to the exact nature of the colloidal constituents of these solutions can be arrived at, the rapid change in viscosity with increasing proportion of silica above the ratio 1:2 points to the probable formation of an aggregate in which the amount of silica increases in a manner analogous to the increase in the value of the ratio SiO_2/Na_2O in the solution itself. This view receives support from the nature of the smooth viscosity-ratio curves discussed above, and from the fact that when the viscosity-concentration curves are considered, those for higher silica content show a rapid rise at lower values of concentration than is the case with the solutions of lower silica content. Thus if an aggregate of the type $(Na_2O.xSiO_2)_n$ were formed in the solution, in which the value of x is in some way dependent on the actual ratio Na_2O:SiO_2 contained in the solution, the solutions containing a higher proportion of silica would be expected to have a considerably higher viscosity value, as the value of x increased, and also to show the rapid rise in viscosity referred to, at a lower value of concentration, the size of the aggregate being greater. This change, however, would be greatly influenced by variations in the value of n. The typically lyophile or emulsoid properties of the solutions, as shown by the viscosity, would also suggest that if such aggregates do exist they are largely solvated. Consideration of the effect of temperature on the viscosity also points to the probability of solvation.

The above remarks are not in any way intended as a quantitative explanation of the behavior of the solutions, viscosity considerations alone being insufficient to show the quantitative nature of the aggregate, or the form in which the silica is present.

The Effect of Temperature on the Viscosity

If the idea suggested above regarding the formation of colloidal aggregates, the nature of which changes with change in silica content of the solution, is correct and the aggregates are associated largely with the solvent, it would be expected that the solutions of high silica content would have a far greater temperature coefficient than those in which the proportion of silica is less.

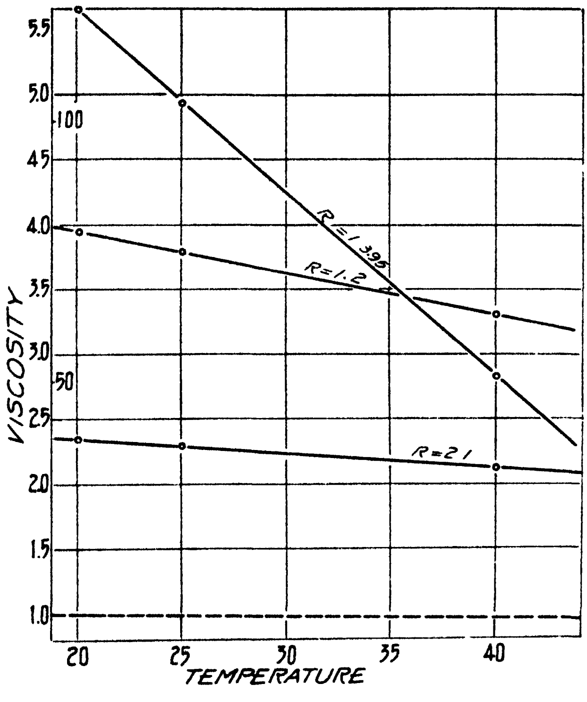


FIG. 13

The effect of temperature on the viscosity of these solutions has been investigated for three ratios Na$_2$O:SiO$_2$ 2:1, 1:2, and 1:3.95, at the concentration 3N$_w$, which is well above that at which the colloidal properties for solutions of ratio greater than Na$_2$O:SiO$_2$ = 1:2 are first exhibited. Values for these solutions have been already given at 25°C., and further values were obtained in the Ostwald instrument at 20°C. and at 40°C. The times of flow for the solutions and for water were obtained at each temperature, and the relative density of each solution at the corresponding temperature was obtained. The results of these measurements appear in Table XXIV, where the values in the fourth column are calculated relative to water at the same temperature. Thus at $T_c°$ the viscosity is given by $\eta_T = t\rho/t_o$ where t and t_o are the times of flow of the solution and of water respectively at $T_c°$ and ρ is the relative density. The maximum error in the series of measurements of time of flow is less than 0.5% in each case, which indicates that the temperature control was adequate. The figures here tabulated are plotted in Fig. 13, viscosity being plotted as ordinates and temperature in degrees centigrade as abscissae. The results for the ratio 1:3.95 are plotted on a much smaller scale than those for the other two ratios, the viscosity values being very much higher, and the effect of temperature greater.

TABLE XXIV

The Effect of Temperature on Viscosity

Ratio $Na_2O:SiO_2$	Temperature $T_c°$	Rel .Density ρ	Viscosity η_o	Viscosity (calc.)
	20	1.1522	2.346	2.348
2 : 1	25	1.1518	2.300	2.298
	40	1.1492	2.148	2.146
	20	1.2194	3.946	3.947
1 : 2	25	1.2190	3.800	3.790
	40	1.2169	3.327	3.319
	20	1.2993	121.60	121.24
1 : 3.95	25	1.2989	103.58	103.43
	40	1.2987	50.12	49.98

Over the range of temperature investigated, the relation between viscosity and temperature is well represented by a straight line, the slope of which increases in a marked way with increasing proportion of silica in the solution. In Fig. 13 the viscosity of water is represented by a straight line parallel to the temperature axis, the viscosity values being expressed in each case relative to that of water at the same temperature. The straight lines are represented by equations of the form:

$$\eta_T = -kT + C$$

or $\eta_T = \eta_o - kT$ where η_T is the viscosity at the temperature $T_c°$ and η_o is that at 0°C. The value of *k* is obtained as the slope of the straight line to the temperature axis and is negative. The value of η_o is obtained as the intercept with the viscosity axis. In the last column of Table XXIV values of viscosity are given, calculated from the above equation, the constants being obtained graphically. The agreement with the experimental values is very close, the difference being always less than 0.3%. The equations for the three solutions investigated may be written:

(a) For Ratio $Na_2O:SiO_2 = 2:1$ $\eta_T = \eta_o - 0.0101\ T$
(b) For Ratio $Na_2O:SiO_2 = 1:2$ $\eta_T = \eta_o - 0.0314\ T$
(c) For Ratio $Na_2O:SiO_2 = 1:3.95$ $\eta_T = \eta_o - 3.562\ T$

Further work is desirable on the influence of temperature on the viscosity of these solutions, but the results, though incomplete, show very definitely the marked increase in colloidal properties of the solutions above the ratio $Na_2O:SiO_2 = 1:2$. The temperature coefficient in passing from the ratio 1:2 to the ratio 1:3.95 shows a very large increase while the change in passing from the ratio 2:1 to the ratio 1:2 is in comparison very small, as is shown by the values of k. The large temperature coefficient of the solutions of high silica content, as shown by these measurements on the solution of ratio 1:3.95, may be explained on the assumption of the formation of a solvated colloidal aggregate. When the temperature is raised, the water held by the aggregate is freed, and a marked fall in viscosity of the solution results.

Summary

The value found for the viscosity of a solution of silicate of soda is dependent on the instrument used for its measurement. Values obtained in an instrument of the Ostwald type are lower than those obtained in one of the variable pressure type. Using the latter, the flow is represented by the equation: $p^n t = \alpha$ and a measure of relative viscosity is given by the value of α/α_o, α_o being obtained for pure water.

Viscosity-concentration curves show the properties characteristic of lyophile sols, and the slope of the viscosity curve at a given concentration is dependent on the ratio $Na_2O:SiO_2$ of the solution, being greater for solutions containing a larger proportion of silica. Viscosity-ratio curves show the influence on the viscosity of additions of silica to caustic soda solutions, the viscosity being increased at first very slowly and then much more rapidly as the proportion of silica is increased above the ratio $Na_2O:SiO_2 = 1:2$ whilst the actual increase in viscosity for a given change of ratio is dependent on the concentration of the solution.

The effect of temperature on viscosity is represented by the linear equation $\eta_T = \eta_o - kT$. The value of the temperature coefficient is greatly influenced by the value of the ratio SiO_2/Na_2O, being higher, the greater the proportion of silica. Below the ratio 2 the change in η_T is small.

It is concluded that solutions containing less silica than is represented by the ratio $Na_2O:SiO_2 = 1:2$ are, at normal concentrations, chiefly non-colloidal, and that when the proportion of silica is higher, a solvated colloidal aggregate is formed, the size and nature of which is dependent on the ratio $Na_2O:SiO_2$ and on the concentration of the solution.

In conclusion the author desires to express his thanks to Professor Donnan, under whose direction this investigation was made, for the interest he has shown in its progress.

The William Ramsay Inorganic and Physical Chemistry Laboratories,
University College, London.

THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN GLYCEROL-WATER MIXTURES*

BY WALTER W. LUCASSE

The transference numbers of an electrolyte can be calculated from the results of measurements of concentration cells without and with liquid junction. In a recent article[1] results have been published from measurements of cells of the type

$$H_2 \mid HCl \mid AgCl \mid Ag$$

in which the acid concentration was varied from 0.001 to 4M in solvents of one and five mole percent. glycerol in water. From these measurements it is possible to calculate the electromotive force of cells without liquid junction of the form

$$Ag \mid AgCl \mid HCl \mid H_2 \mid HCl \mid AgCl \mid Ag$$

In the present paper are given results of measurements of liquid junction cells of the type

$$Ag \mid AgCl \mid HCl\ (m) \mid HCl\ (0.01\ M) \mid AgCl \mid Ag$$

in solutions of one and five mole percent. glycerol at 25° ± 0.01. The acid concentration was varied from 0.01 to 1 M.

The hydrochloric acid and glycerol were the same as used in the previous study and the solutions and electrodes were made up in the same manner. The cell used was similar to that described in a previous investigation[2], the only change being that the capillary tube connecting the parts B and C was made in the form of a U-tube thus further decreasing the possibility of concentration changes in the solution around the electrode in part C due to diffusion.

The results are given in Table I, the values of the electromotive force being the mean of a number of readings taken over a period of several hours after the cell had been allowed to stand in the thermostat for about five hours. The variation in the readings was extremely small, seldom more than a few hundredths of a millivolt. Measurements were also made in each solvent with the electrolyte at 0.001, 0.002 and 0.005 M. The variations between duplicate determinations were found, however, to be large and from the cells without liquid junction it was seen that the type of electrode used is unreliable at low concentrations. The results of all measurements between 0.01 and 1 M are given with the exception of one at 0.02 M in the second series which was obviously in error. In the first series the values of the electromotive force at 0.1 and at 1 M are each the mean of two determinations, the average deviation from the mean being 0.14 and 0.08 mv., respectively. The

---

* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] J. Am. Chem. Soc., **48**, 626 (1926).

[2] J. Am. Chem. Soc., **47**, 743 (1925).

TABLE I

Results from Liquid Junction Cells
Ag | AgCl | HCl (m) | HCl'(0.01 M) | AgCl | Ag

	Solvent: One mole % glyc.			Solvent: Five mole % glyc.		
m	E	log A	t_+	E	log A	t_+
(0.001)		−0.0195	0.814		−0.0191	0.845
(.002)		+ .2792	.817		+ .2746	.844
(.005)		.6656	.821		.6594	.843
.01	0.00000	.9552	.825	0.00000	.9469	.842
.02	.02812	1.2420	.828	.02846	1.2345	.841
.05	.06511	1.6160	.832	.06530	1.6075	.840
.1	.09259	1.9020	.834	.09433	1.8893	.839
.2	.12090	2.1841	.838	.12165	2.1726	.838
.28	.13507	2.3257	.840	.13574	2.3152	.838
.38	.14811	2.4566	.841	.14894	2.4477	.838
.5	.15994	2.5769	.843	.16057	2.5664	.837
.7	.17565	2.7327	.844	.17671	2.7259	.837
1.0	.19306	2.9085	.846	.19422	2.9036	.836

value at 1 M in the second series is the mean of two determinations, the average deviation from the mean being 0.07 mv. The concentrations are expressed in terms of formula weights per 1000 grams of solvent.

The method used in calculating the transference numbers was that employed by MacInnes and Beattie[1]. For a uni-univalent electrolyte the equation relating the activity of the electrolyte and the electromotive force of a cell without liquid junction is

$$d\,E = \frac{2\,R\,T}{F}\,d \ln a_\pm \qquad (1)$$

and for a cell with liquid junction

$$d\,E_t = t_+ \frac{2\,R\,T}{F}\,d \ln a_\pm \qquad (2)$$

If the electromotive force be plotted against the logarithm of the geometrical mean activity a straight line will result from the first equation, of constant slope, $\frac{2\,R\,T}{F}$; while a curved line of variable slope, $t_+ \frac{2\,R\,T}{F}$, will result from the second equation since t_+ is a variable. The ratio of the slopes of these lines at any given activity yields the cation transference number at the corresponding concentration. The values of the electromotive forces of the cells without liquid junction were related to the values of $\log 10^3\, a_\pm (= \log A)$, obtained from the cells without liquid junction, by the empirical equation

$$E_t = a + b(\log A) + c(\log A)^2$$

The values of the constants *a*, *b* and *c* were determined by the method of least squares.

---

[1] MacInnes and Beattie: J. Am. Chem. Soc., 42, 1117 (1920).

For the one mole percent. solution the equation obtained was

$$E_t = -0.092528 + 0.096289\ (\log A) + 0.00066196\ (\log A)^2 \quad (3)$$

and thus the slope of the curve was

$$\frac{dE}{d\ (\log A)} = 0.096289 + 0.0013239 \log A$$

Dividing by the constant slope of the curve without transference (1) gave for the variation of the transference number

$$t_+ = 0.8139 + 0.01119 \log A \quad (4)$$

The mean deviation, positive and negative, of the observed values from those calculated by equation (3) was 0.11% of the total electromotive force.

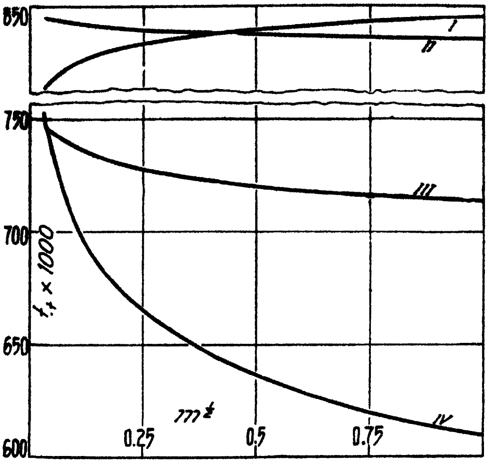


Fig. 1

The Cation Transference Numbers of Hydrochloric Acid: I in one mole percent glyc., II in five mole per cent glyc., III in fifty mole per cent alcohol, IV in absolute alcohol.

For the five mole percent. solution the equation obtained was

$$E_t = -0.094589 + 0.099982\ (\log A) - 0.00018642\ (\log A)^2 \quad (5)$$

and thus for the transference numbers

$$t_+ = 0.8452 - 0.003152 \log A \quad (6)$$

The mean deviation, positive and negative, of the observed values from those calculated by equation (5) was 0.18% of the total electromotive force.

The values of the transference numbers given in Table I were computed from equations (4) and (6). The values of log A there given are, with the exception of those at 0.001, 0.002 and 0.005 M, from the observed results of the activity coefficient determined from the cells without liquid junction. The values of log A at the bracketed concentrations were obtained from the calculated values of the activity coefficient and the corresponding values of the transference numbers were computed by assuming that the validity of equations (4) and (6) may be extended to these concentrations, although the equations were formed from the data between 0.01 and 1 M inclusive.

The distribution of the curves may be seen from Figure 1 where the cation transference number × 1000 is plotted against the square root of the molality. There are plotted also, for comparison, the values found by Harned and Fleysher[1] for the cation transference numbers of hydrochloric acid in 50 mole percent. alcohol and in absolute alcohol. According to the "best values" of Noyes and Falk[2] the cation transference numbers of hydrochloric acid in water at 18° rise from 0.832 at 0.005 normal to 0.844 at 1 normal. At 25° the values are doubtlessly about 1% lower and rise in about the same manner or perhaps with slightly greater rapidity. It will be noted that the transference number of the hydrogen ion increases with increasing acid concentration in the one mole percent. glycerol solution while in the other three solvents it decreases, the decrease being more rapid the smaller the water content. The distribution of the curves indicates a similar behavior at constant acid concentration to that found by Krumreich[3] for the cation transference numbers of 0.01 normal silver nitrate in mixtures of ethyl alcohol and water at 40°. The transference number of the silver ion was found to increase from 0.482 in pure water to 0.488 in 30% alcohol after which it decreased rapidly to 0.410 in 99.8% alcohol. Had the glycerol content been greater in the present study the curve would doubtlessly have decreased much more rapidly than in the five mole percent. solution and given values of the transference numbers considerably lower than those in water. It is conceivable that measurements in alcoholic solutions of higher water content would give values of the cation transference number which would rise with increasing acid concentration and, indeed, would be greater than those in pure water at the same concentration. Such behavior may be attributed to changes in the relative solvation of the ions in the different solvents.

Summary

Measurements at 25° of cells of the form

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}\ (m) \mid \mathrm{HCl}\ (0.01\ M) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

in which m is given a number of values up to one molal in solvents of one and five mole percent. glycerol, have been presented.

From these data and the results from corresponding cells without liquid junction, the cation transference numbers of hydrochloric acid have been calculated.

Philadelphia, Pennsylvania.

---

[1] Harned and Fleysher: J. Am. Chem. Soc., **47**, 92 (1925).

[2] Noyes and Falk: J. Am. Chem. Soc., **33**, 1436 (1911).

[3] Krumreich: Z. Elektrochem., **22**, 446 (1916).

NEW BOOKS

The Chemical Action of Ultraviolet Rays. *By Carleton Ellis and A. A. Wells. 23 × 16 cm; pp. 362. New York: Chemical Catalog Company, 1925. Price: $5.00.* The chapters of this interesting book are entitled: introduction—nature of ultraviolet radiation; sources of ultraviolet rays; metal vapor lamps—mercury arc lamps; protective glasses and filters; observations on photochemical mechanism; reactions of gases in ultraviolet rays; various photochemical and photolytic reactions—general and inorganic; photochemical and photolytic reactions—organic (2); the effect of ultraviolet rays on halogenation reactions; photosynthesis—the formation of carbohydrates and proteins from atmospheric gases; sterilization by ultraviolet rays; biologic effects and therapeutic applications—experimental studies (2); miscellaneous applications of ultraviolet rays.

"At the present time much interest is displayed in what may be termed the photoequivalence law of Einstein and the radiation hypothesis of Lewis-Perrin. Photochemists are now striving not so much for the accumulation of facts on the synthesis and photolysis of chemical bodies as they are to establish the laws which govern the union and disunion of the elements and their compounds under the action of radiation. The establishment of laws governing such changes would make it possible to predict in a large number of cases the outcome of radiation of a given character. There is no question therefore of the importance of investigations tending to confirm the Einstein and Lewis-Perrin proposals or to replace these by others which may better fit the facts. Aside from the foregoing it should be noted that the principal fields of study and investigation which are now occupying the attention of photochemists are the synthesis of carbohydrate and protein material by the aid of light or ultraviolet radiation, the improvement of monochromatic light sources and the production of cold light. This last-mentioned subject is of great practical interest as our modern methods of producing light for heating bodies to incandescence is decidedly wasteful. The production of light without heat and therefore the elimination of the loss of energy due to radiated heat would of course represent a revolutionary step. Considerable progress has been made by Harvey and others in the field of luminescence and phosphorescence through a study of living creatures capable of emanating cold light, such for example as the firefly or glow-worm. These subjects, however, take us beyond the scope of the present volume. The other topic of investigation mentioned above, namely the improvement of monochromatic light sources, is beginning to receive a considerable measure of attention and many developments in this direction during immediate coming years are predicted. With better means for research, such as is likely to be afforded through refinements in apparatus giving radiation of definite and limited wave-length, the possibilities of photosynthesis and photolysis will be greatly expanded," p. 18.

"A mercury arc lamp is described by Heraeus which has a tungsten anode placed at such a distance from the mercury as to maintain permanency of the arc even at high pressures and with great resistance. In this lamp a ten-fold increase in brightness corresponds to a twenty-fold increase in the ultraviolet radiation in the neighborhood of $366\mu\mu$ and there is smaller consumption of energy and a more permanent length of arc than with carbon arc lamps," p. 50.

"According to some authorities the production of cataract may be at least partially due to the action of rays of short wave-length which have been proven to give rise to a certain turbidity of the eye lens, when present in large quantities. In particular it has been suggested that the prevalence of cataract among glass workers might be explained in this way. Schanz and Stockhausen have declared that ordinary glasses, and even those constructed of blue glass, fail to stop the ultraviolet rays of the most dangerous nature.

"While developing certain blue glasses Luckiesh noticed that cobalt glass appeared to be more transparent than clear glass to ultraviolet rays in the neighborhood of $300\mu\mu$. Conclusive evidence was obtained by means of clear and blue glasses (soda-lead) of (1) equal thickness and (2) of the same content except that the blue glass contained in addition a very small percentage of cobalt. Clear and blue specimens of the same thickness were compared in pairs by photographing the spectrum of the quartz mercury arc through each. These experiments established the fact that the glass containing the slight amount of cobalt was more transparent to the mercury lines near $300\mu\mu$. Since this observation was first made it has appeared to Luckiesh that certain blue glasses which have been developed chiefly for scientific purposes owed a portion of their usefulness to this augmented transparency in the region of $30c\mu\mu$," p. 74.

"Luther and Goldberg have shown that oxygen acts as an inhibitor in all photochlorinations, and they consider that the effect is due to absorption by oxygen of radiation re-emitted by the chlorine, which would promote the reaction if not thus absorbed. Bodenstein extends the inhibiting effect of oxygen to all secondary photochemical reactions, except those in which oxygen itself takes part," p. 98.

"The dissociation of hydrogen in low-voltage arcs was observed by Duffendack and Compton not to take place below a minimum voltage of 13 but above 16 volts the rate was rapid, decreasing to 65 volts. Dissociation from contact with the hot filament was always superimposed on the electrical dissociation. With mercury arcs, the dissociation was several times more rapid, the hydrogen molecules presumably being activated by excited mercury atoms.

"Dickinson notes that hydrogen and oxygen in contact with mercury combine to form water at 45°C. or even at room temperature, when illuminated by rays from a quartz mercury arc lamp cooled by a blast of air. This is said to be due to dissociation of the hydrogen by collisions with mercury atoms excited by absorption of the mercury line 253.7 uu. In the absence of any one of the three substances or of the exciting radiation, no reaction takes place," p. 101.

"The decomposition of ozone by light in presence of chlorine has been studied quantitatively by Weigert, the rays of a quartz mercury lamp being used, and the rate of decomposition being measured by means of the change of pressure of the gas. There is no induction period, and decomposition stops when the gas is cut off. The rate of decomposition is independent of the concentration of the chlorine and it is nearly proportional to the intensity of the light. By placing a vessel containing chlorine between the source of light and the ozone tube, a measurement of the quantity of light absorbed by the chlorine is obtained. In this way Weigert showed that the rate of decomposition of the ozone is proportional to the quantity of light absorbed by the chlorine mixed with it. It is suggested that the light produces some intermediate product which is destroyed rapidly by the action of ozone," p. 107.

Coehn and Becker find that at 160° the conversion of sulphur dioxide into sulphur trioxide is only sixty-five percent and not one hundred percent, there having been a very large displacement of the equilibrium, p. 116.

"Plotnikow has expressed the opinion that every element or compound which has a free valence electron is photochemically unsaturated, that the photoactivity is a periodic function of their atomic numbers, and that every photochemically unsaturated compound is photoactive. Light tends to convert the unsaturated into the saturated, and in the process energy may be either absorbed or evolved. In general the longer light waves influence the reactions in which there is a loss of energy, and the short waves those in which there is a gain. A photochemically inactive system may be made active by the addition of such substances as uranium, iron, and chlorine which are rich in valence electrons and which act as catalyzers. These are classified as contact, transfer, chemical, and optical catalysts depending upon the manner in which they enter into reaction. According to Nazarov photochemical effects are now usually regarded, at least as far as their initial stages are concerned, as photoelectric effects, and since the latter are independent of the temperature, and since, further, the velocity of a photochemical reaction depends on the mass of the activated molecules, and this on the velocity of activation, if follows that the temperature-coefficients of photochemical processes should be less than those of reactions occurring in the dark. It appears probable that the temperature-coefficient of a photochemical reaction is of a magnitude characteristic of the structure of the photochemical component which absorbs the light. Thus in the absorption of light by the molecules containing, as photochemical components, iodine or bromide, the temperature-coefficients have the same value, 1.40," p. 120.

"Curtis states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury lamp, neither are they bleached by the addition of three per cent hydrogen peroxide to them until the mixture is rayed. To be sure that the bleaching was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to radiation while a stream of oxygen was bubbled in but there was no bleaching in this case, hence it appears that the oxidizing power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to rays of short wave-lengths. On the other hand, Holmes reports that solutions of magenta, malachite green, methyl violet, and crystal violet, which have been decolorized by sulfur dioxide, when exposed to ultraviolet of wavelength between $220\mu\mu$ and $330\mu\mu$ develop their original colors. Comparison of the absorption spectra of the original dyes and those which had regained the color showed that the regained color is due to the original dye, since the absorption spectrum is the same in both cases. The reaction with sulfurous acid is reversible and consists of a decolorizing action and a colorizing action, the latter being photochemical. The large quanta of energy supplied by the ultraviolet rays cause the photochemical action to increase and consequently a displacement of the position of equilibrium occurs. The equilibrium position can also be displaced by chemical and thermal means," p. 125.

The change in color of minerals and glasses, "under the influence of radium rays is in many cases the outcome of a reducing action while the ultraviolet rays have an oxidizing action; consequently ultraviolet and radium rays frequently induce opposite changes." The ultraviolet transparency of certain colored media is of interest from the standpoint of absorption. Absalom makes the observation that many gems and minerals which in ultraviolet rays are transparent when colorless, do not lose their transparency in the colored specimens; nor is any effect noted on artificially coloring a specimen by means of cathode rays, although colored metallic salts and aniline dyes are opaque. This is strong evidence that the color of minerals is due to colloidal metals, especially in such cases as hyacinth (zircon) and yellow topaz. Deeply colored solutions of the alkali metals and magnesium in liquid ammonia also are extremely transparent in the ultraviolet, which tends to show that these metallic solutions are colloidal," p. 135.

"In view of the effect of colored light upon plant growth and pigmentation, Gardner suggested a study of the precipitation of lithopone under colored light or ultraviolet radiation. Believing that the coloration of zinc oxide in lithopone might be due to the presence of zinc sulfide, Nishizawa mixed zinc sulfide and glycerol on paper and exposed it to the action of ultraviolet rays. There was no coloration of the zinc compound and it was found by similar experiments that other polyatomic alcohols have the same protecting properties. Certain organic salts such as zinc tartrate and Rochelle salts have a like effect, while some others are without influence. Magnesium and calcium hydrate also serve as protectors to the zinc compounds. It was shown that linseed oil and turpentine have no effect on this protective action, and that only minute quantities are necessary to afford complete protection. Based on the above experiments a new method of manufacture of lithopone was devised, in which the zinc sulfide is treated with glycerol, or the saccharides, and salts and esters of tartaric and polyhydroxystearic acids. The sulfide may be incorporated with the organic compound itself, or with its aqueous solution. The sulfide may be precipitated in the presence of the organic compound, or the organic compound may be formed in the presence of the zinc sulfide. Prepared in this manner the sulfide shows no appreciable change when exposed for several hours to the action of ultraviolet rays or by gradually heating to a temperature of 120°C," p. 138.

"Some relation is to be expected between the absorption spectrum of a substance and its photochemical activity. According to Henri and Wurmser, the latter depends solely on that part of the absorption spectrum coinciding with the atomic groups affected by photochemical action. The rest of the light energy absorbed appears as heat. This gives the possibility that photochemical decomposition may differ with different wave-lengths, depending on the groups responsible for absorption. Thus Bielecki and Henri were able to break up the absorption curves of aldehydes and ketones into simple elementary curves. Aldehydes gave two and ketones three curves. They conclude that rays of different wave-lengths are absorbed by different groups," p. 142.

"The polymerization products [of vinyl esters], which form more or less rapidly in accordance with the intensity of illumination and the temperature, are solid, colorless, and transparent, celluloid-like masses which are odorless and can be turned, cut, planed, and otherwise manipulated to form various articles. These solids, rendered plastic in hot water, can be molded and, upon cooling, the material becomes hard again. Chlorinated esters may be polymerized by heat and light as a two-stage operation in the following manner: 1 kilogram of vinyl chloracetate is mixed with from 0.5 to 1 gram of benzoyl peroxide and carefully heated in a large vessel provided with a reflux condenser. At from 80° to 100° polymerization takes place, while the temperature rises rapidly. At this time care should be taken to cool the reaction vessel. The violence of the reaction may be modified by diluting the reaction liquid with an indifferent solvent; for instance, in the present example, about 300 grams of chlorobenzene can be used. The reaction product is a viscous syrupy mass which can be further treated by exposing to light without a diluent, solid masses being obtained as the remaining, unaltered vinyl ester polymerizes. The syrupy solution or a solution made from the completely polymerized ester may be used as a lacquer or other coating compound. When allowed to dry in thin layers, colorless films of a celluloid-like nature are said to be obtained. Vinyl chloride may be polymerized by ultraviolet rays, but the product derived is not as satisfactory as that obtained from the esters mentioned. According to Kuhl the polymerization of vinyl esters (vinyl acetate or vinyl chloroacetate) by ultraviolet light yields solid masses which may serve as substitutes for celluloid and which are fireproof and odorless. The polymerization is assisted by catalytic agents (organic peroxides) to give thick syrups which on illumination give solid masses having valuable properties," p. 151.

"According to Maynard the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If mercurous iodide is used with methyl iodide, methyl mercuric iodide is formed rapidly. The action of metallic mercury is confined almost entirely to methyl iodide. The use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide," p. 151.

"A detailed study of the photolysis of acetaldehyde has been made by Berthelot and Gaudechon who state that ultraviolet rays of long wave-length do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid. The amount of acid produced is far greater when the aldehyde is in the form of vapor than when it is liquid. With rays of wave-length $250\mu\mu$ polymerization is rapid, both para and meta acetaldehyde being formed. No resinification results from the action of long ultraviolet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerization and resinification, but favors acidification, formic acid produced in this case and in amount almost equal to that of the acetic acid. Of three compounds studied, viz.: acetaldehyde, ethyl alcohol and acetic acid, only acetaldehyde is decomposed by sunlight (wave-length greater than $300\mu\mu$). Rays from a mercury lamp screened by thin glass which absorbs all rays of wave-lengths less than $300\mu\mu$ decompose acetaldehyde in accordance with the equation $CH_3.CHO = CO + CH_4$. Frequently the proportion of methane to carbon monoxide actually found is somewhat less than corresponds to this equation, for the light causes polymerization of some of the aldehyde to paraldehyde which is then photolyzed to carbon monoxide and ethane or more complex substances. These latter reactions are most readily produced by the extreme ultraviolet rays."

"According to Berthelot and Gaudechon simple sugars may be divided into four classes according to their resistance to light; ketoses are attacked by ultraviolet rays $\lambda = 300\mu\mu$, the aldoses by the rays $\lambda = 300$ to $250\mu\mu$, the straight chain polyhydric alcohols by rays $\lambda = 250$ to $200\mu\mu$, the ring polyhydric alcohols only by the ultraviolet of wave-length $200\mu\mu$. With the longer radiations producing the first stage in the action, the liquid remains neutral and does not reduce Fehling's solution in the cold. With decreasing wave-length decomposition increases, the liquid becomes acid, and carbon dioxide can be detected in the gaseous products, the amount of hydrogen evolved increases and the solution begins to reduce Fehling's solution in the cold, finally, methane is liberated. The volumes of carbon monoxide and hydrogen evolved in the first stage always bear a simple ratio to one another," p. 159.

"The influence of light upon various acids and their salts is interpreted by Jaeger and Berger largely by ionic equations, and from the results it is concluded that each photochemical reaction is specific and very dependent upon conditions obtaining at the moment, so that it is scarcely ever possible to predict its course. Among the conditions governing the reaction the presence of certain ions in the solution must be considered a factor of great importance. In the photochemical decomposition of salts the velocity of reaction is greatly influenced by the presence of certain cations in the solution. The addition of certain neutral salts first increases the velocity and on further addition retards it or completely stops it. The greater the electrical charge of the cation of the salt added, the smaller the quantity required to bring the rate of decomposition to a maximum, p. 165.

"The leuco-bases of Brilliant Green, Malachite Green, Crystal Violet, Rhodamine B, 3B and 6G, also leucaniline and "leuco blue," are sensitive to the respective complementary colors of the dyes and may be used for actinometric purposes. Mixed with collodion they are more light-sensitive than the dyed silver bromide and silver chloride films hitherto used in photometry. As it is sensitive to ultraviolet, according to Eder the leuco-base of Brilliant Green is specially suited for use in plant physiology experiments, being sensitive to that part of the spectrum which is active in chlorophyll formation," p. 193.

"From a study of the assimilatory quotient CO_2/O_2 Willstätter and Stoll contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be unity; that is, for each volume of carbon dioxide absorbed one volume of oxygen is liberated. In the formation from carbon dioxide of formaldehyde the quotient is 1.0; for glycollic acid 1.33; for formic acid 2.0; and for oxalic acid 4.0," p. 222.

"As to the actual part which chlorophyll plays in the photosynthesis of carbohydrates in the living plant, Thatcher points out that three possible modes of action are now receiving experimental study. The first of these, which has naturally been longest considered as the probable function of chlorophyll, is that it acts chemically as a catalyst by forming unstable intermediate products with formaldehyde or possibly other simple intermediate compounds of the photosynthetic process. Indeed, several investigators have shown that chlorophyll actually does form a compound with formaldehyde from which complex the formaldehyde may be either given off or absorbed in order to establish a proper equilibrium in the photosynthetic process, and to afford in the plant a mechanism by which the quantity of free formaldehyde is regulated. In this way the amount present in free form at no time reaches that which would be toxic to the cell protoplasm. The second of these conceptions is that, regardless of the color and of the general chemical reactivity of chlorophyll, the mineral constituent (magnesium) which it contains is held in proper colloidal form to exert a definite catalytic effect upon the photosynthetic process. The third, and most recent, explanation of the mechanism of chlorophyll action is that the pigment acts as a photocatalyst, or light screen, to absorb and transmit the energy from light rays of the proper wave-length to accomplish the several steps in the photosynthesis of carbohydrates," p. 231.

"We have already learned that the ultraviolet component of solar radiation at the earth's surface is practically identical with the region which is possessed of stimulative action and which is not endowed with lethal power. In other words, living beings on the face of the earth have, at least partially, adapted themselves to exposure to rays of wave-lengths not shorter than $300\mu\mu$. No natural occasion has arisen to evolve a mechanism protective against the shorter waves; these, therefore, preserve their fatal effect on living beings.

"The fact that our protection against the solar ultraviolet is incomplete has led Woodruff to suggest that our remote ancestors evolved in dark, cloudy regions, where such rays could reach the earth in only feeble amounts. The surmise may be correct, but it is at least as easy to suppose that the advantages of the stimulative action outweighed the relatively unimportant ill effects, and that excess of the latter was countered by the development of pigment," p. 272.

"Gebhard has confirmed the theory that the bleaching of dye solutions or of dyed tissues by light is due to the primary formation of a peroxide of the dye. The peroxide is best detected by acidified potassium iodide and starch, by alkaline potassium permanganate, or by diphenylamine and concentrated sulphuric acid. Chromic, molybdic, and titanic acids do not indicate the presence of a peroxide, which fact furnishes one of Gebhard's several arguments against the primary formation of hydrogen peroxide. The rays which are most effective in the production of the peroxide are those complementary to the color of the dye. Blue, violet and ultraviolet rays exert a decomposing action on the peroxide, or occasion a transference of the active oxygen to unattacked molecules of the dye. Gebhard utilizes Mumm's theory of oxidation in the presence of water and shows by an electrolytic experiment that the perhydroxyl-ions are instrumental in bleaching the dye," p. 313.

Wilder D. Bancroft

The Constitution of Matter. *By Max Born. Translated by E. W. Blair and T. S. Wheeler. 22 × 15 cm; pp. vii+80. New York: E. P. Dutton and Company, 1923. Price: $2.50.* The subject is presented under three general headings: the atom; from mechanical ether to electrical matter; the fusion of chemistry and physics. On the first page the author says: "The modern theory of the atom has its origin in chemistry. Physicists have turned only slowly and reluctantly to the atomic point of view, and while atoms and molecules have long been in daily use by the chemist, it is but a short time since there were physicists who regarded the atomic theory as a sometimes seemingly useful, but in the main avoidable, hypothesis. It is not so to-day. The physicist, helped by the investigations of the last few years, may now presume to instruct the chemist in the nature and the actions of the atom. For physical methods penetrate deeper into the atom than do chemical; while the speculations of chemists on the structure of atoms and the forces at work between them, especially as regards valency, were somewhat arbitrary, being chiefly based on one manifestation of atomic force—chemical combination, the idea of the atom as conceived by present-day physicists is, in many vital respects, free from such arbitrariness. One can be confident that future investigation will amplify, but at the same time leave, the clear outline that we now know."

We encounter adsorption even when determining the value of the quantum, p. 7. Ehrenhaft of Vienna worked with considerably smaller drops than Millikan used and believed that he had detected much smaller charges. "More recent experiments, particularly those of Regener and his collaborators and of Bär suggest, however, that the phenomena observed by Ehrenhaft cannot be explained by a subdivision of the elementary charge, but are due rather to the adsorption of gases on the surfaces of the minute spheres, which then appear to possess abnormally small densities."

"As we have already seen, the lattice of the [rock-salt] crystal is not composed of NaCl molecules, but of individual Na and Cl atoms. This is proved, not only by Laue's X-ray photographs, but also by the thermal behavior of the crystal. The energy of a body consists in the motions of its smallest constituents; in crystals, these vibrate about their centres of gravity. According to a fundamental law of statics, the energy of these vibrations is divided amongst the individual constituents so that in time each and every constituent possesses *the same* amount of energy which can be determined from the kinetic theory of gases. From thermal measurements one can deduce the number of particles, each containing this amount of energy, which must be present in unit mass, so that this may contain the observed heat-content. In this way it was proved that the constituents cannot be NaCl molecules, for the unit mass would then contain only half as many particles, and consequently only half the observed heat-content, as it would if they were atoms," p. 42.

"If such a NaCl solution is evaporated so that the rock-salt crystallises out, the process consists of the individual Na and Cl atoms uniting to form the above-mentioned lattice. What happens then to the charge of the atoms; do these cancel one another, or do the atoms retain their ionic character in the solid state as well?

"Madelung has answered this question by the interpretation of an optical property of crystals such as NaCl. Imagine a piece of rock-salt placed between two parallel, charged, metal plates; then the lattice is exposed to an electrical field. If we assume that the Na atoms are positively, and the Cl atoms negatively, charged then the former will be attracted in the direction of the field, and the latter in the opposite direction. Owing to the rigidity of the crystal, this attraction will produce only a very small relative displacement of the Na and Cl ions. Now consider the well-known phenomenon of resonance: if a pendulum is allowed to oscillate freely in its natural period, the amplitude can be increased with a minimum of work. In the same way, an oscillating electrical field of suitable period will cause a maximum displacement in the crystal. Light-waves are such oscillating electrical fields; it is to be expected, therefore, that light of a suitable wave-length will appreciably affect the crystal, and *vice versa* be affected by it. Rubens has proved this; he found that infra-red light of a very long and definite wave-length is strongly reflected by the crystal, whilst light having a slightly different frequency is unaffected. By repeated reflections he was able to isolate this selective light, and on this account called it the "residual rays."

"These residual rays proved that the atoms of the crystal were charged. That this charge for crystals of the type NaCl is exactly one electron, has been shown by calculating the known frequency of the light from the charge of the electron, the masses of the ions and the measurable elastic forces of the crystal.

"Recently, however, the ion-charge has been tested directly by Debye and Scherrer, by means of X-ray photographs. The X-rays perturb the electrons of the atom, thus producing secondary rays, which proceed from the atom; these, by reason of their interference produce the phenomena discovered by Laue. The intensity of the interference spots will depend on the number of electrons present in the atoms; conversely, by measuring the intensity of the interference spots, conclusions can be drawn as to the number of electrons the atom contains. In this way it has been shown that, in the crystal of lithium fluoride, the Li atom has one electron less, and the F atom one more, than in the neutral state. Similar conditions undoubtedly exist in all compounds of the alkali metals (Li, Na, K, Rb, Cs) with the halogens (F, Cl, Br, I)," p. 44.

Nernst's third law of thermodynamics is considered by the author as indeed "a great achievement—the determination of chemical processes by purely physical measurements. It is a fusion of chemistry with physics, which apparently leaves nothing to be desired.

"But there yet remains another problem, the solution of which must always be an ideal of the physicist—the proof of the unity of all physical and chemical forces and their reduction to reactions between the elementary components of matter—electrons and atoms, or atom-nuclei. Modern physics already possesses models of the atom, which certainly approximate to the facts, and with these it can explain numerous mechanical, electrical, magnetic, and optical phenomena. It must not stop with these, but must endeavor also to reduce chemical properties to atomic forces, in so far as they are known. In this respect Nernst's theory is a good starting-point, for it reduces the complexity of chemical processes to a series of simple constants. It is now the task of the molecular physicist to calculate from the properties of the atom these constants which the physical-chemist can determine by calorimetric and similar measurements. This opens up an extensive field of thermochemical investigation," p. 51.

"When we contemplate the path by which we have come we realize that we have not penetrated far into the vast territory of chemistry; yet we have travelled far enough to see before us in the distance the passes which must be traversed before physics can impose her laws upon her sister science," p. 78.

Wilder D. Bancroft

Three Centuries of Chemistry. *By Irvine Masson. 14 × 21 cm; pp. 191. London: Ernest Benn, 1925. Price 10 shillings, 6 pence.* The French savant who described chemistry as a French science, founded by Lavoisier, would certainly have refused to go back to the seventeenth century for the initial development of modern chemistry. Without doubt, however, as Professor Masson shows, the basis of this wonderful structure is to be found in the philosophy of Francis Bacon and the experimental work of Robert Boyle. The present volume on broad philosophic lines and characterized by much literary skill, deals in some detail with that new spirit of investigation which became manifest in England in the first half of the seventeenth century and which somewhat later led to the founding of the Royal Society.

It was Boyle, one of the original Fellows, whose work first showed the value, in the realm of chemical phenomena, of direct experimental evidence in contrast with so-called discoveries, made by reason or argument alone. As the author says: "Boyle dragged chemistry out of a welter of sophisms and charlatanry, endowed it with life and ideals and material, and set it forward upon the true path."

The predominance of the phlogistic hypothesis during the greater part of the eighteenth century was not so much an aberration from this true path, as a continuance of the ways of thought which Boyle and his school had striven to counteract. Professor Masson maintains that in his attitude towards chemical phenomena, although not in time, Lavoisier was the immediate successor of Boyle, whilst Stahl and his disciples were really the heirs of the old spagyrical mentality. "If Boyle's '*Sceptical Chymist*' is for chemistry the Book of Genesis, Lavoisier's '*Traité Elementaire*' is its Book of Exodus, for it shows how he led his people out of a captivity that has endured for nearly a century."

The slow progress made during the eighteenth century towards clarity on such fundamental matters as calcination and combustion is faithfully portrayed, and the contributions of the leading workers—Black, Cavendish, Priestley, Scheele, and Lavoisier—are set forth in detail. The significance of Lavoisier's appeal to the balance is emphasised, as is also the effect of his work in finally disposing of the old 'elements.' "The union [of fuels] with atmospheric air which had been discovered so long ago, and which phlogistians admitted to occur as a merely secondary event ensuing upon an efflux or transfer of phlogiston, was now proved to be the primary event: the union was further narrowed down to one widely distributed simple substance, oxygen, and the relic of the element of Fire was at last recognized as an illusion. With it had vanished the Elements of Water and Air and Earth, so that the ancient stronghold invested by Boyle was finally carried by assault by Lavoisier."

The period of 1800-1925 is handled by the author on quite different lines. No attempt is made to enter into detail and attention is concentrated on 'the search for the structure units' which has characterized so much of the chemists' work during the last century and a quarter. The physical molecule, the chemical molecule, the atom, and the ion are the topics round which the discussion centres and the gradual evolution of definite ideas in regard to these units, their assembly and interplay, is sketched in an extraordinarily able way Professor Masson's historical studies convince him of the impossibility at the present time of separating the spheres of physics and chemistry: "there is now only one Physical Science, to which physicists and chemists variously contribute: and perhaps the outstanding intellectual achievement of our time is that which enables such a statement to be justified."

J. C. Philip

Factory Practice in the Manufacture of Azo Dyes. *By W. B. O'Brien. 23 × 16 cm; pp. viii+176. Easton: The Chemical Publishing Company, 1924. Price: $5.00.* "A factory process is merely a routine based upon theoretical and experimental considerations. The soundness of chemistry indispensable in theoretical and research work must be inherent in factory processes, but, apart from chemistry, economy in regard to labor and materials and conformation to the limitations of the short working day becomes of paramount importance. A lay belief somewhat generally accepted attributes an indefinable, mysterious elusiveness to the work of dyestuff production. Such belief, while serious enough in the stubbornness with which it persists, is in no way justified. Similarly to other large industries, success in dyestuff manufacturing depends upon capital, organization and hard work. The advantage possessed, elsewhere than in America, due to earlier participation in the industry, has been largely compensated by economic and circumstantial factors affecting the industry here," p. 3.

"The time required for the completion of a coupling reaction in the factory depends much upon the efficiency of the contact obtained between the diazo and component. In case both are completely soluble, reaction may be completed immediately after mixing, or at the most within a few hours. In the cases of slightly soluble diazos and components, used in suspension, as much as forty-eight hours' agitation of their mixture may be necessary to completely utilize the one present in lesser amount. Efficient agitation and a fine state of division in the reacting materials promotes the contact and is necessary for completing the coupling reaction. The less soluble diazos are to be had in a finely divided condition as a result of the method of their preparation, but a process should include directions for producing this state for slightly soluble components used in suspension. The volume or concentration of the coupling mixture influences the progress of the reaction differently for individual cases. Some azo dyes on formation precipitate immediately in a thick slimy state of particles which hinder contact between unreacted portions of the diazo and component and completion of such coupling is favored by efficient agitation rather than by concentration, but in cases where the resulting dye is very soluble, or else precipitates in a crystalline form, concentration is advantageous," p. 4.

"In the manufacture of azo dyes the unit quantity of the production is the batch or charge. For practical work the batches prepared should be of a size sufficient to yield from 500 to 1,000 pounds of dye, selling strength, in a single charge. On such a scale the production can be of sufficient volume to carry the manufacturing expense, while the size of the batches is not too great for good control and completion within twenty-four hours," p. 14.

"The most of the azo dyes are marketed in a powder form, hence the wet product of the making building must be dried and pulverized. Drying of any batch of dye consumes more time than does the work of coupling and filtering; a charge may be completely coupled in twenty-four hours and filtered within another twenty-four hours for each set of tubs and filters, but drying for the same charge will require from four to eight days. Adequacy of facilities for drying permits of speed in production," p. 33.

"The general run of azo colors is not considered explosive, more dangerous members of the class having become less used, but some azo dyes are known to ignite and burn with a smoldering flame during drying or milling; the Alizarine Yellows, R and GG, are often mixed with three percent ammonium sulfate before entering into the ovens, to prevent possible ignition," p. 36.

"Common salt is mixed with direct dyes and dyes which are to be applied in a sulfuric acid bath, including the mordant dyes and acid dyes; also with basic azo dyes. Sodium sulfate is mixed with dyes which are to be applied in a bath acidified with acetic acid, such as the "sulfon" colors. A dyestuff may be marketed in several strengths, such as the "ordinary", and the "concentrated," with greater, or less, reduction in the milling. Certain of the "highly concentrated" wares consist of unreduced dye, the manufacture being directed with a view to obtaining as pure a product as possible, with less regard for yield and cost in the production. Reduction of dyes is not considered adulteration or falsification but is an operation necessary for obtaining a consistently standard product, due to the fact that no two batches run to similar strengths as first prepared. Discrepancy in the strengths of dyes marketed for the same brand by different manufacturers comes from a difference in standards adopted, but the products of one factory can be expected to be in accordance with the standards announced by that factory. There is nothing, however, to prevent a purchaser from remilling and further reducing the dye for resale; the appearance of dye does not indicate the general extent to which reduction has been made, and only a laboratory test of each package can show the actual strength of the dye," p. 37.

"In the manufacture of dyes and intermediates the number of professionally trained employees required to carry on the work forms a high percentage of the total help, as a result of the technical and varied character of the work. The circumstance has been dwelt upon, in the educational advertising campaigns of dye manufacturers, that as a matter of experience rather than point of view a minimum ratio of one professionally trained chemist to ten operators is compatible with successful production. The chemistry of a factory process allows the possibility of varied results, similar to a laboratory experiment. While for the azo dyes the mechanical features of a process, such as the filtration, drying and milling, may be regulated and conducted in the factory by non-professional operators, the chemical nature of the "making" operation resists standardization to the extent that every factory charge is in degree an experiment whose course must be followed by a chemist as for a laboratory experiment," p. 166.

The chapters are entitled: introduction; buildings, major equipment, operation, materials; diazotization of aniline; dyes prepared from diazotized aniline; diazotization of the homologues of alcohol; diazotization of the nitro anilines; diazotization of the sulfonated anilines; diazotization of acetyl paraphenylene diamine and anthranilic acid; mono azo dyes from ortho amino phenol derivatives; mono azo dyes from alpha naphthylamine and naphthionic acid; mono azo dyes from amino naphthol sulfonic acids; tetrazotization of benzidine; relation of the chemist to the industry—experimental work and small scale production. *Wilder D. Bancroft*

Les Méthodes physiques appliquées à la Chimie. *By P. Job. 22 × 14 cm; pp. viii+251. Paris: Gaston Doin et Cie, 1926. Price: 30 francs.* This is the fourth volume of a series of monographs on Physics and Chemistry published under the direction of Professors Langevin, Perrin, and Urbain.

It is a well written, clear and systematic exposé of the circumstances and the manner in which various physical measurements can afford assistance to the chemist. The nature of the chemical problem is first considered and then the physical methods applicable to the case. The general principles of each method are set forth very well with the help of numerous diagrams but without going into details. In practically all instances the methods are illustrated by actual cases culled from the literature and this is one of the best features of the book. With hardly any exceptions, all the physical methods which have been applied to chemical problems are dealt with as well as a few which seem as though they might be helpful although they have not actually been used as yet.

The book does not aim at supplying the minute details necessary for the successful application of the methods described, although a brief description of the methods of making the various measurements is given in an appendix. For fuller details the reader is referred to numerous text-books and to a wide and judicious selection of international literature.

The experienced reader will, perhaps, find little new in the book but, all the same, it is one that he might well read with pleasure and with profit. It would be a useful book for an English-speaking student to read who wished to improve his knowledge of French, and degree students might be encouraged to read it, especially as the price is low.

It is very free from misprints, only one of any consequence having been noticed—on page 197 where the first half of line eight from the bottom has been repeated in the second half of the line. There is a good index.

The general scheme of the book may be gathered from the following summary of the matters dealt with. It is divided into two parts, each of six chapters.

Part one is concerned with Pure Substances and successive chapters deal with: (1) Identification of pure substances and determination of their purity; (2) Qualitative and quantitative analysis; (3) Molecular weight of gases, dissolved substances, liquids, and solids; (4) Atomic weights; (5) Constitution of pure substances; (6) Allotropic forms.

Part two deals with mixtures, solutions, and heterogeneous systems; and the six chapters consider: (1) Determination of the individual substances present; (2) Constitution of solid mixtures; (3) Constitution of liquid mixtures which are in equilibrium; (4) Constitution of gaseous mixtures which are in equilibrium; (5) Reacting chemical systems; (6) Foretelling reactions. These twelve chapters account for 183 pages of the book and in addition there are a brief introduction and conclusion the Appendix of 50 pages, index and table of Contents. *H. Bassett*

Organische Chemie. *By R. Pummerer. Second enlarged and improved edition. 22 × 15 cm; pp. x+210. Dresden and Leipzig: Theodor Steinkopff, 1923. Price: 90 cents.* The subdivisions are organic valence problems; coal and tar dyes; the study of natural products. The chapters are entitled: metallo-organic compounds; radicals; thermo-chemistry, spectrochemistry, absorption spectra; colored, unsaturated compounds; oxonium salts and betains; readily reacting sulphur compounds; compounds with twin double bonds; keto-enol isomerism; ennobling coal; dyes and intermediates; methods of oxidation and hydrogenation; hydrogenated carbocyclic compounds; sugars; anthocyans; tanning materials; enzymes and hormones; alkaloids; blood pigments, chlorophyll, assimilation.

The possible catalytic action of glass is well illustrated, p. 61, by the fact that keto-acetyl-dibenzoylmethane can not be made to give a melting-point of 107° when tubes of Jena glass are used. The oxidation of ethylene to formaldehyde can only be carried out successfully when the ethylene is stabilized by dilution with fairly large amounts of nitrogen, p. 83. Connstein and Lüdecke have found, p. 132, that the yield of glycerol can be increased from three percent to 10-16% by alkaline fermentation of sugar. Addition of neutral sodium sulphite cuts out the danger of lactic acid fermentation and increases the yield of glycerol to 36% of the sugar taken. During the war the Germans made glycerol commercially by fermentation of a sugar-rich molasses. This process cannot compete at present prices with the usual one for obtaining glycerol from fats.

Pentagalloylglucose probably occurs in Turkish tannin which on hydrolysis yields five mols of gallic acid to one of glucose. The Chinese tannin contains approximately twice as much gallic acid (ten mols) to one of glucose as the Turkish tannin does, p. 157.

Leaves free from chlorophyll do not assimilate; but yellow-leaved varieties, poor in chlorophyll, show unexpectedly strong powers of assimilation and consequently there is no proportionality between the chlorophyll content and the power of assimilation, p. 191. Variations in light and heat affect the yellow leaves quite differently from the green leaves and consequently Willstätter and Stoll conclude that there is another substance besides chlorophyll which is of importance in producing assimilation.

While chlorophyll forms a true solution in alcohol, it goes into colloidal solution in water. From the absorption spectrum and from the reaction with carbon dioxide, it seems certain that the chlorophyll in the green leaf is in colloidal and not in true solution.

Wilder D. Bancroft

Ueber Kolloidchemie. *By R. Zsigmondy. Second edition. 20 × 13 cm; pp. 53. Leipzig: Johann A. Barth, 1925. Price: 3.60 marks.* This is a new edition of a lecture given in 1906 at Stuttgart with some additional foot-notes. It is really quite surprising how little change is necessary in order to make it a perfectly satisfactory lecture today. This does not mean that there has been no progress in nearly twenty years because that would be absurd. It merely means that a lecture dealing primarily with facts and not with theory does not necessarily ever go out of date. Except that we don't differentiate sharply any more between suspension colloids and emulsion colloids, the presidential address of A. A. Noyes before the American Chemical Society at Philadelphia would be just as interesting today as when it was given. It could be adapted to modern use with only minor changes in the presentation.

The references in the foot-notes giving the changes are chiefly to Zsigmondy's own book which is probably good advertizing.

Wilder D. Bancroft

A RELATIONSHIP BETWEEN ATOMIC NUMBERS AND THE PROPERTIES OF IONS IN THE CRYSTAL LATTICE.

II. The Characteristic Frequency and the Constraint*

BY ARTHUR F. SCOTT

In order to account for the properties of crystalline solids on the basis of the modern lattice theory it has been found necessary to postulate two distinct forces, one, an attractive force of an electrostatic nature, and the other, an opposing or repellent force that is not of a purely electrostatic nature. It should be mentioned in this connection that the pioneering speculations of Professor T. W. Richards in this field, embodied in his suggestive theory of the compressible atom, led directly to the same conclusion. Professor Richards distinguishes the attractive force as chemical affinity, "a force which binds atoms together", and the other force as "an inherent distending tendency." Further, both conceptions of the solid state agree in a very important particular in that they recognize the fact that these forces are characteristic of the atoms themselves. Or, to restate this idea in the language of the lattice theory, ions in a crystal lattice cannot be treated as point charges; in short, it must be recognized that ions have definite, characteristic structures which control the action of their external forces, attractive and repellent alike. Although it is known that the structures of atoms depend upon their atomic numbers and that therefore the forces under consideration must likewise be related to the atomic numbers, very little progress has been made toward solving the problem in terms of the ultimate factors. It is the object of this paper to present preliminary considerations which may afford some insight into this rather involved problem.

For this purpose we shall make use of the characteristic frequencies of solids; which term, as we shall use it, signifies the definite, upper limit of the infrared spectrum as defined by Debye[1]. Ordinarily this physical constant of solids must be determined directly from measurements of heat capacity, although in the case of salts, it can also be determined from measurements of residual rays. But because the experimental data, thermal and optical, which are essential for the evaluation of the characteristic frequency are so scant, recourse must be had to the various indirect methods that have been suggested. Inasmuch as we shall have to employ computed values of the characteristic frequency subsequently, it will be profitable to digress at this point in order to examine the source of our material.

Of the various indirect methods which have been suggested, the formula proposed by Lindemann[2] is generally considered to be the most satisfactory, especially in respect to the metallic elements, and is expressed by the equation:

$$\nu = 2.80 \times 10^{12}\sqrt{T/MV^{2/3}} \qquad (1)$$

---

* Contribution from the Department of Chemistry of Reed College.

[1] Debye: Ann. Physik, (4) **39**, 789 (1912).

[2] Lindemann: Physik. Z., **11**, 609 (1910).

where ν is the frequency; T is the melting-point temperature; M and V are the atomic weight and volume of the substance. This formula was originally deduced from the assumption that at the melting point the amplitude of vibration of the atoms about their position of equilibrium is equal to the distance between them. In spite of the improbability of the above mechanism, we may still accept the formula for our present purpose because the identical expression has been developed from dimensional considerations[1].

From the viewpoint of our present knowledge concerning the structure of crystalline solids, there is, however, a rather obvious alteration to be made in the statement of the above formula. It is no longer necessary to employ the $V^{1/3}$ term as a measure of the distance between ions in a solid; rather it would seem advisable and more accurate to make use of the "nearest approach" of ions in a crystal lattice as determined by crystal structure analysis. With this change equation (1) assumes the form:

$$\nu = \text{const.}/d_o\sqrt{T/M} \qquad (2)$$

where d_o is the "nearest approach" and the constant is chosen arbitrarily. In this paper the constant will always be taken as equal to 3.83×10^4.

Table I is presented to show the effect of such an alteration. Column (1) contains the values for the frequency calculated according to equation (2) for which the essential data are given in Table II. The values obtained from equation (1) are given in column (2) and are taken from Mellor[2]. In column (3) we have the experimental values as determined from thermal data. These values are taken from a compilation by Eucken[3]. The figures for zinc, sulfur, and iodine are taken from a table of Nernst and Lindemann[4] and are the frequencies used in their formula. Although not exactly comparable to the other values, they are approximate enough to give some idea of the magnitude of ν. Furthermore, as Debye has shown, the characteristic temperature of solids may be determined from the elastic constants of the substance. Making use of these values of the characteristic temperature, Allen[5] has calculated ν for the elements given in column (4).

A scrutiny of the contents of Table I shows that the results of equation (2) are notably in better accord with the experimental values than those obtained by equation (1). This statement is particularly true for those elements possessing a structural arrangement other than a "face" or "body-centered" cubic lattice, for example, the diamond. When one takes into account the arbitrary temperature at which d_o is measured and the fact that the melting point temperature employed does not always correspond to the melting point of the modification existing at ordinary temperature, it is somewhat surprising that

---

[1] Einstein: Ann. Physik, (4), **35**, 689 (1911); Grüneisen: (4) **39**, 257 (1912); Verh. deutch. Ges., 13, 836 (1911).

[2] Mellor: "Treatise on Inorganic and Theoretical Chemistry", **1**, 829.

[3] Eucken: "Gründriss physik. Chemie", 83, 102.

[4] Nernst and Lindemann: Z. Electrochem., **17**, 822 (1911).

[5] Allen: Proc. Roy. Soc., **94A**, 100 (1917).

TABLE I

A Comparison of the Characteristic Frequencies obtained from Various Sources

Element	1 Calc. Eq. 2.	2 Calc. Eq. 1.	3 Thermal Debye	4 Elastic Consts.
Diamond	43.1 × 10^{12}	31.7 × 10^{12}	39.00 × 10^{12}	
Aluminium	7.85	7.70	8.30	8.26 × 10^{12}
Phosphorus	9.71	6.12		
Sulfur	6.47	3.92	7.3	
Argon	1.49		1.74	
Iron	8.81	8.30	9.45	9.67
Nickel	8.39	8.07		9.01
Copper	6.74	5.88	6.60	6.81
Zinc	4.67	4.35	4.8	
Silver	4.49	4.36	4.50	4.39
Cadmium	2.98	2.74	3.50	3.48
Iodine	2.38	1.66	2.0	
Platinum	4.68	4.36		4.68
Gold	3.47	3.36		3.44
Lead	1.88	1.66	1.83	1.49
Bismuth	1.99	1.64		2.30

the agreement is so close. Because of its greater accuracy as well as its dimensional correctness, equation (2) will be used hereafter in preference to equation (1).

In anticipation of the needs of the subsequent discussion, ν has been calculated for all the elements for which relaible data are available; and the results are given in Table II. In order to condense the tabulation as much as possible, the values for the atomic weights are not included but these constants are the accepted ones, having been taken from the recent report of the Atomic Weight Committee[1]. Also no definite references are given for the melting point temperatures selected, but in practically every case they have been taken from Landolt-Börnstein's Tabellen. A review of the literature has prompted a few deviations from the figures given in the Tabellen. A further word in explanation of the data seems desirable. In order to supplement the meagre data from X-ray analysis a number of values for d_o were computed in the usual manner from the atomic volumes of the elements. In all of these cases the value for the density employed in the calculation is taken from Landolt-Börnstein's Tabellen; and the type of lattice assumed was in each particular instance determined by the types of lattices known for the neighboring elements in the periodic table. The figure for vanadium was also computed in this manner because the X-ray data could not be considered reliable enough. The data attributed to Bragg come from his computation of the radii of combination and have been used when all other sources failed. The basic assumption is of

---

[1] J. Am. Chem. Soc., 47, 597 (1925).

Table II

The Characteristic Frequencies of Elements

e = maximum number of valence electrons.
Z = atomic number.
M.P. = melting point in degrees absolute.
d_o = "nearest approach" of atoms in crystal lattice, in Angstroms.
ν = characteristic frequency $\times 10^{-12}$.
m = atomic weight.
k = constraint.

Element	e	ln(Z+e)	M.P.	d_o	Type of Lattice Known or Assumed.	ν	$k^{\frac{1}{2}} \simeq m^{\frac{1}{2}}\nu$.
H	1	0.693	15		dens. = 0.0763	4.51	4.51
He	2	1.386	Ca. 2	2.93	F.C.C.[1]	2.94	5.88
Li	1	1.386	167.85	3.03	B.C.C.[2]	10.28	27.1
Be	2	1.792	1551	2.28	Hexagonal[3]	21.83	65.6
B	3	2.079	2800	1.86	Hypothetical[4]	33.13	109.0
C	4	2.303	Ca.3600	1.54	Hexagonal[5]	43.1	149.0
F	7	2.773	50	1.35	Hypothetical[6]	4.60	20.1
Ne	8	2.890				(2.0)[7]	8.9
Na	1	2.485	370.9	4.00	B.C.C.[2]	3.845	18.4
Mg	2	2.639	923	3.22	Hexagonal[2]	7.33	36.1
Al	3	2.773	931.7	2.860	F.C.C.[8]	7.85	40.8
Si	4	2.890	1686	2.35	Tetrahedral cubic[2]	12.63	66.9
P	5	2.996	863	2.08	Hypothetical[6]	9.71	54.1
S	6	3.091	384	2.05	Hypothetical[6]	6.47	36.6
Cl	7	3.178	172.1	2.10	Hypothetical[6]	4.02	23.9
A	8	3.258	84	3.73	F.C.C.[1]	1.49	9.4
K	1	2.996	336.5	4.48	B.C.C.[8]	2.51	15.7
Ca	2	3.091	1082	3.93	F.C.C.[9]	5.05	32.0
Sc	3	3.178				(7.0)[7]	46.6
Ti	4	3.258	2061	2.90	Hexagonal[10]	8.65	60.0
V	5	3.332	1983	2.89	B.C.C.[11]	8.26	59.0
Cr	6	3.401	1793	2.508	B.C.C.[12]	8.97	64.7
Mn	7	3.466	1533	2.55	B.C.C.[1]	7.93	58.7
Fe	8	3.526	1806	2.472	B.C.C.[8]	8.81	65.8
Co	8	3.555	1751	2.514	F.C.C.[12]	8.30	63.7
Ni	8	3.584	1725	2.474	F.C.C.[8]	8.39	64.3
Cu	1	3.401	1355.8	2.543	F.C.C.[8]	6.74	53.8
Zn	2	3.466	692.3	2.670	H.C.P.[12]	4.67	37.7
Ga	3	3.526	302.8	3.03	F.C.C.[1]	2.63	22.0
Ge	4	3.584	1231	2.43	Tetrahedral cubic[13]	6.49	55.3
Se	6	3.689	473.2		dens. = 4.82	3.39	30.2
Kr	8	3.784	104	3.97	F.C.C.[1]	1.08	9.6
Rb	1	3.638	312	4.93	B.C.C.[1]	1.49	13.7
Sr	2	3.689	1102	4.33	F.C.C.[1]	3.14	29.4
Y	3	3.738	1523	3.80	B.C.C.[1]	4.17	39.3
Zr	4	3.784	1803	3.18	Hexagonal[10]	5.36	51.1

TABLE II (continued)

Element	e	ln(Z+e)	M.P.	d_0	Type of Lattice Known or Assumed.	ν	$k^{\frac{1}{2}} \simeq m^{\frac{1}{2}}\nu$.
Cb	5	3.829	2223	2.95	B.C.C.[1]	6.35	61.3
Mo	6	3.871	2840	2.720	B.C.C.[8]	7.66	75.0
Ru	8	3.932	2223	2.640	Hexagonal[12]	6.78	68.4
Rh	8	3.970	2243	2.700	F.C.C.[12]	6.62	67.2
Pd	8	3.989	1822.2	2.729	F.C.C.[8]	5.80	59.9
Ag	1	3.871	1233.5	2.884	F.C.C.[8]	4.49	41.6
Cd	2	3.912	593.9	2.96	H.C.P.[12]	2.98	31.5
In	3	3.951	427	3.24	Tetragonal F.C.[12]	2.28	24.4
Sb	5	4.025	903	2.87	Rhombohedral[14]	2.89	31.9
Te	6	4.060	725.5		dens. = 6.25	2.45	27.6
I	7	4.094	386.5		dens. = 4.933	1.66	18.7
Xe	8	4.127	133	4.14	F.C.C.[1]	0.94	7.6
Cs	1	4.025	301.45	5.34	B.C.C.[1]	1.01	11.6
Ba	2	4.060	1123	4.52	F.C.C.[1]	2.42	28.4
La	3	4.094	1083	3.75	F.C.C.[1]	2.85	33.6
Ce	3	4.111	908	3.64	F.C.C.[10]	2.68	31.7
Pr	3	4.127	1213	3.71	F.C.C.[1]	3.02	35.9
Nd	3	4.143	1113	3.65	F.C.C.[1]	2.92	35.0
Ta	5	4.357	3071	2.833	B.C.C.[12]	5.56	74.9
W	6	4.382	3660	2.732	B.C.C.[8]	6.25	84.8
Os	8	4.431	2773	2.66	Hexagonal[10]	5.49	75.8
Ir	8	4.443	2628	2.690	F.C.C.[12]	5.25	73.0
Pt	8	4.454	2037	2.766	F.C.C.[8]	4.68	62.5
Au	1	4.382	1336	2.874	F.C.C.[8]	3.47	48.7
Hg	2	4.407	234		dens. = 14.383	1.26	19.2
Tl	3	4.431	576	3.38	F.C.C.[15]	1.90	27.2
Pb	4	4.454	600.4	3.479	F.C.C.[8]	1.88	27.0
Bi	5	4.477	544	3.11	Rhombohedral[14]	1.99	28.8
Rn	8	4.543	202	4.01	F.C.C.[1]	0.91	13.6
Th	4	4.543	1973	3.54	F.C.C.[10]	3.15	48.1
U	6	4.585	1623	2.00	B.C.C.[1]	3.40	52.4

The types of arrangements have been abbreviated as follows: face-centered cubic (F.C.C.), body-centered cubic (B.C.C.), hexagonal close-packed (H.C.P.).

---

[1] Calculated.
[2] Hull: Phys. Rev., **10**, 661 (1917).
[3] McKeehan: Proc. Nat. Acad. Sci., **8**, 270 (1922).
[4] From graph by author: J. Phys. Chem., **29**, 304 (1925).
[5] Debye: Physik. Z., **18**, 291 (1917).
[6] Bragg: Phil. Mag., (6) **40**, 169 (1920).
[7] From Figure 1.
[8] Davey: Phys. Rev., **25**, 753 (1925).
[9] Hull: Phys. Rev., **17**, 12 (1921).
[10] Hull: Phys. Rev., **18**, 88 (1921).
[11] Hull: J. Franklin Inst., **193**, 189 (1922).
[12] Hull: Phys. Rev., **17**, 571 (1921).
[13] Kolkmeyer: Proc. Roy. Acad. Sci., Amsterdam, **21**, 405 (1919).
[14] Ogg: Phil. Mag., **42**, 163 (1921).
[15] Becker and Ebert: Z. Physik, **16**, 165 (1923).

course that in the pure element two ions can never come closer together than twice the radius of combination. That the points fit so well on the following graph indicates the approximate correctness of Bragg's premises. To obtain the atomic volumes of the inert gases, the densities employed were those calculated by Herz[1] according to the method of Lorentz[2] and are the hypothetical values at absolute zero. According to Simon and von Simson[3], solidified argon forms face-centered cubic crystals; consequently the values for d_o for all of the inert gases have been calculated from the atomic volumes at absolute zero, assuming that this structure is correct. Finally the values of ν for a few elements have been computed by equation (1) because this seemed to be the only way available. These data are also included in Table II.

In addition to the characteristic frequencies of the elements, we shall subsequently have need also of the same constants for a group of comparable salts. The simplicity of structure and especially the completeness of the requisite data of the alkali halides make these salts singularly suitable for our purpose. However, when it comes to the question of selecting some indirect method by means of which we can calculate the frequency, the obvious intrinsic differences in the nature of salts and metals offers adequate warning that we cannot hope for the same formula to apply with equal validity to the two types of substances. That there is a substantial basis for this statement will, it is hoped, be implicitly demonstrated in the course of this paper. As a matter of fact, Lindemann's formula, equation (1), although it does give results of the proper magnitude, is by no means as accurate as the dimensional formula proposed by Madelung and Einstein[4]. The latter may be written:

$$\lambda = C\chi^{\frac{1}{2}}M^{\frac{1}{3}}\rho \qquad (3)$$

Here λ is the wave-length; χ, the compressibility; and ρ, the density. C is a constant which, when calculated from the residual-ray wave-length of sodium chloride, has the value; 1.162×10^8 sec.$^{-1}$; and M is computed from the atomic weights, M_1 and M_2, of the two ions according to the formula:

$$M = \frac{(M_1M_2)}{(M_1 + M_2)} \qquad (3a)$$

The frequency is obtained, of course, by dividing the velocity of light by the wave-length. The following Table III will serve to illustrate the relative validity of the two formulae.

---

[1] Herz: Z. anorg. Chem., **105**, 171 (1919).

[2] Lorentz: Z. anorg. Chem., **94**, 240 (1916).

[3] Simon and von Simson: Naturwissenschaften, **11**, 1015 (1923).

[4] Madelung: Physik. Z., **11**, 898 (1910); Einstein: Ann. Physik, **34**, 170, 590 (1911); **35**, 679 (1911).

TABLE III

A Comparison of the Characteristic Frequencies obtained from Various Sources.

Salt	1 Residual-Ray.	2 Thermal.	3 Calc. Eq. 1.	4 Calc. Eq. 3.
NaCl	5.77×10^{12}	5.87×10^{12}	6.37×10^{12}	$(5.77) \times 10^{12}$
KCl	4.73	4.80	5.10	4.80
KBr	3.63		3.76	3.73
KI	3.19		2.93	3.08

Column (1) contains the results of Rubens[1] and his students from optical measurements. The values for the frequency obtained from thermal data are given in column (2) and are taken from the compilation by Eucken which was already been mentioned. In column (3) we have the recent calculations of Herz[2] made by means of equation (1); it should be noted, however, that for these calculations he employed the density of the salts at the melting point temperature on the assumption that in the Lindemann equation ν is a function of the melting point. Even though this device improves the results considerably, for example, giving the value of ν for sodium chloride, 6.37×10^{12}, instead of the previous value, 7.2×10^{12}, it can be seen at once that the results do not agree so well as in the case of the elements. The results from the Madelung-Einstein formula as calculated by the author are presented in column (4) and are taken from Table IV. A comparison of the figures in the above Table shows, as Born[3] has pointed out, that equation (3) is doubtless the correct dimensional formula for salts.

Hence, the frequency, ν, has been calculated for the alkali halides which have the same structure as rock-salt. The essential data and results are given in Table IV.

The data given in Table IV are taken from various sources. The density values of the chlorides, bromides, and iodides of sodium, potassium, and rubidium for 0°C. are taken from a paper by Baxter and Wallace[4]. The same constants for the corresponding lithium salts at 25°C. are from measurements by Baxter[5]. Spangenberg[6] has published the values for the fluorides with the exception of rubidium fluoride. This last figure, as well as the compressibility data for sodium, potassium, and rubidium fluorides has been taken from a computation made by the aurthor[7] according to the method proposed by Fajans and Grimm[8]. The compressibility figures for lithium and potassium

---

[1] Rubens: Sitzungsber. königl. preuss. Akad., **1917**, 47.

[2] Herz: Z. anorg. Chem., **128**, 135 (1924).

[3] Born: "Atomtheorie des festen Zustandes", 625.

[4] Baxter and Wallace: J. Am. Chem. Soc., **38**, 259 (1916).

[5] Baxter: J. Am. Chem. Soc., **31**, 558 (1904).

[6] Spangenberg: Z. Kryst., **57**, 494 (1923).

[7] Scott: J. Phys. Chem., **29**, 304 (1925).

[8] Fajans and Grimm: Z. Physik, **2**, 299 (1920).

TABLE IV

The Characteristic Frequencies of the Alkali Halides

$(Z_c - Z_a)$ = the absolute value of the difference of the atomic numbers of the cation and anion.

χ = the compressibility in bars × 10^{12}

ρ = the density at 0°C.

k = constraint.

$$m = \frac{4\,m_1 m_2}{m_1 + m_2}$$

ν = characteristic frequency × 10^{12}.

Salt	$\ln(Z_c - Z_a)$	ρ	χ	ν	$k^{\frac{1}{2}} \simeq m^{\frac{1}{2}}\nu$
LiF	1.792	2.640	1.53	13.7	61.8
LiCl	2.639	2.068	3.7	9.21	44.4
LiBr	3.446	3.464	5.0	7.81	39.5
LiI	3.912	4.061	7.2	6.71	34.4
NaF	0.693	2.808	2.6	7.88	50.8
NaCl	1.792	2.168	4.3	(5.77)	43.1
NaBr	3.178	3.213	5.3	4.73	41.7
NaI	3.738	3.677	7.1	4.07	38.0
KF	2.303	2.491	3.31	5.33	38.1
KCl	0.693	1.992	5.2	4.80	40.8
KBr	2.773	2.756	6.4	3.73	36.9
KI	3.527	3.133	8.8	3.08	34.9
RbF	3.332	3.722	6.1	4.62	36.3
RbCl	2.996	2.806	7.3	3.57	35.7
RbBr	0.693	3.358	8.2	2.69	34.6
RbI	2.773	3.560	9.3	2.34	32.7

fluoride are taken from determinations by Slater[1]. The remaining compressibility data are those recently published by Richards and Saerens[2]. Obviously, as the foregoing description of the data indicates, too much confidence should not be placed in the computed values of the characteristic frequency.

Returning to our main thesis we find that, apart from its application to the phenomenon of specific heat, the characteristic frequency has received but little consideration, notwithstanding the fact that there are several reasons for believing it to be closely related to the non-mechanical properties of the elements. For instance, we have Haber's "square-root" rule[3] which, although based upon a too great simplification of the probable conditions, is exceedingly exact; and it can be interpreted only on the assumption that the forces which hold the ions together in a lattice are identical with the forces which control the peripheral, or valence, electrons. Moreover, that the characteristic frequency, like most of the other physical properties of the elements, is intimately related to the atomic number is demonstrated by the Lothar Meyer type curve obtained by Biltz[1] and the interesting, although unexplained relationship of Allen[2]. The relationship to the atomic numbers is not so surprising when one takes into consideration the fact that the melting point temperatures and atomic volumes, of which according to equation (1) the frequency is a function, are properties exhibiting a periodic variation with the atomic number. At this point, in order to avoid any subsequent misunderstanding, it should perhaps be pointed out that the above periodicity is clearly associated with the valences of the elements. Consequently we may expect that, along with the atomic numbers, the valence electrons are also responsible for the nature of atomic properties. All of this suggestive evidence, moreover, may be taken as sufficient grounds for believing that a definite connection exists between the characteristic frequency and the other properties of the elements, particularly those forces to which we ordinarily attribute chemical behavior. If this is true of the elements, it may likewise be true of salts, even though we have no direct evidence on the subject.

---

[1] Slater: Phys. Rev., (2) **23**, 488 (1924).

[2] Richards and Saerens: J. Am. Chem. Soc., **46**, 934 (1924).

[3] Haber: Verh. deutsch. physik. Gesell., **13**, 1117 (1911).

The first requirement towards an understanding of these facts would necessarily be the restatement of the above qualitative relationship in a quantitative form. At the outset our inquiry is met with the difficulty that there is no information available on this point. Indirect evidence, however, concerning the relationship between the characteristic frequency and the atomic numbers may be adduced in the following fashion. Imagine a case where the frequencies of the inert gases (as solids of course) are expressed by some function of Z (atomic number) and e (valence electron), which we will write as usual,

$$\nu = f\,(Z,e) \tag{4}$$

Passing to the adjacent group of elements in the periodic table, the alkali metals, we may picture their crystal lattices as consisting of positive ions, without attempting to place the valence electron in any definite position. If these positive ions have electronic structures identical to those of the corresponding inert gases, then the sole noteworthy difference between the members of these two groups lies in the fact that Z for each alkali metal is greater by one than each of the corresponding inert gases. In order to discover the effect of this uniform increase in the atomic number on the obscurely related frequency, let us next imagine the simplest possible condition, namely, that this increase in the atomic number affects the indefinite function (4) as a whole. If this is so, we may express this uniform variation of the function by a constant factor or parameter, α, as follows:

$$\nu = \alpha\, f(Z,e) \tag{4a}$$

---

[1] Biltz: Z. Elektrochem., **17**, 676 (1911).

[2] Allen: Proc. Roy. Soc., **94A**, 100 (1917).

The ions of the elements of the second, third, and possibly fourth group are likewise assumed to have an electronic structure similar to the corresponding inert gases. Hence, by the same reasoning, we can conceive of other factors, β, γ, and δ in place of α, expressing the effect of an increase of two, three, or four in the atomic numbers corresponding respectively to the second, third, and fourth groups of elements in the periodic table. Without attempting to define more precisely the form of our function, we can nevertheless readily test our assumption, for it is easy to see that the frequencies of the alkali metals should be expressible as a linear function of the frequencies of the inert gases, where the slope of the line is equal to α. The lines of the other three groups plotted in a similar manner should likewise be linear functions with their respective parameters as tangents.

That such a condition is realizable can be seen from Fig. 1 where this device has been employed. In this particular example, however, it was considered expedient to take the frequencies of the alkali metals as determinant points on the abscissa, but this fact obviously has no effect on the interpretation of the diagram. The data for this graph can be found in Table II. With the exception of the point for aluminium, the thermal value of which is indicated by a black dot, this mode of portrayal is accurate well within the limits of experimental error. Concerning the gross discrepancy of the aluminium value, it can only be remarked that the same discrepancy recurs in all subsequent considerations; and the hypothetical value, 10.66, (indicated by a cross), appears always to be satisfactory as the normal one.

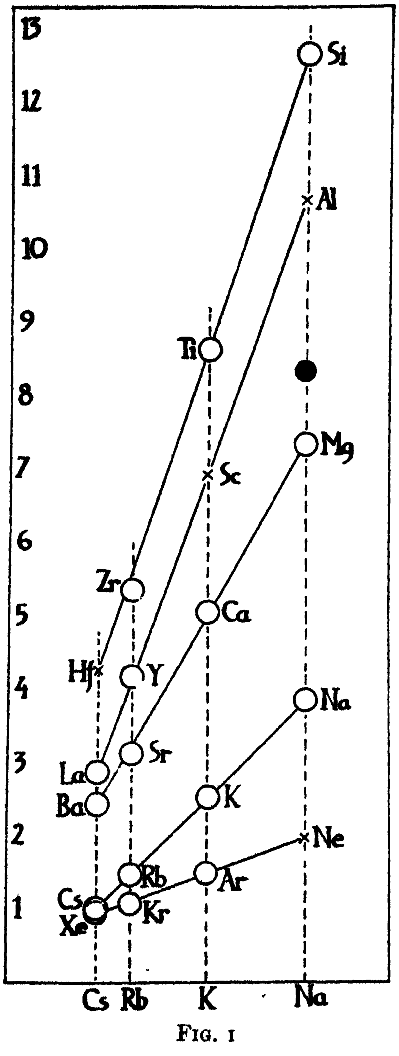


Fig. 1
Frequencies of Elements plotted against Frequencies of Alkali Metals.

In order to furnish an indication of the accuracy of the above mode of representation, it was found necessary to draw Fig. 1 on such a large scale that the points for the elements of the first period could not be included. Consequently the points for these elements have been calculated and the values are subjoined. For the sake of comparison the "observed" values of Table I are also given.

	Li	Be	B	C
calculated.	(10.28)	18.32	28.39	30.64
observed.	10.28	21.83	33.13	43.1

The agreement is not very close. If the basic premise is accepted, there are two explanations which may be offered as to the cause of this disagreement. Either the above considerations do not extend to ions with the electronic structure of helium, or else the determinant point for lithium is at fault. An examination of the latter possibility shows clearly that it has no foundation.

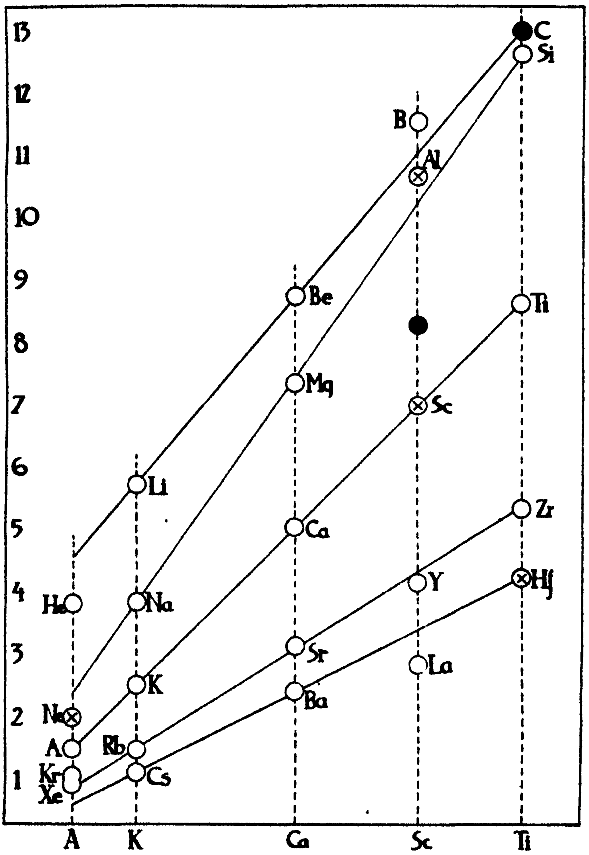


FIG. 2

Frequencies of Elements plotted against Frequencies of Elements of the Third Period.

But before coming to any definite conclusion regarding the behavior of the elements with an ionic structure similar to that of helium, it will be instructive at least to reverse the above procedure as has been done in Fig. 2. Here it has been found convenient to use the values of the frequencies for the elements of the third period as the determinant points for the abscissa. The value used for scandium is the hypothetical one determined from Fig. 1. In order to accommodate the elements of the first period to the graph, their frequency values have been divided by four and then increased by approximately three.

Before analyzing the information afforded by this diagram, the irregular behavior of the elements of the third group should be accounted for. The difficulty hinges on the value of scandium used as the determinant point. If a value slightly greater than the hypothetical one should be used, the points for boron, aluminium, and scandium would all fall on one line; if, on the other hand, a slightly smaller value should be used, the heavier elements and scandium would be on a straight line. The fact that the scandium point should be so irregular is not particularly disturbing because it is more or less expected on the basis of the Bohr theory. Since this matter will be treated more in detail later, the discussion of its application may be postponed for the present. With this situation understood, we may summarize the information offered by the two diagrams as follows: The characteristic frequency of the elements is a function of the atomic number and of the number of valence electrons, which last factor distinguishes different groups. This function varies with each group and period by some characteristic, constant parameter. This statement is possibly subject to three limitations: first, the elements of the first period deviate from this rule in their relation to the elements of the same group; second, the inert gases in their relation to the adjacent metallic elements are doubtless also exceptions; and third, in the case of the third group elements a marked discontinuity makes its appearance with scandium.

When the elements with an ionic structure other than that of an inert gas are treated in the same manner as those already discussed, we obtain unambiguous idication of regularities identical with those shown in the first two figures. But no similar representation is offered for these elements because their data are less certain and also less suited to the purpose of a graph.

If our guiding idea is correct, that the characteristic frequencies of solids are determined by the so-called chemical forces, it is only natural to expect the other class of polar compounds, the salts, to follow a somewhat similar rule. For there is essentially no great difference in the structures of these two classes of substances. We may, for instance, believe that potassium chloride is similar to metallic potassium with the chlorine ion substituted for the valence electron. Under these conditions the results should be the same if one compares a series of alkali chlorides with the other corresponding series of alkali halides because then we should be comparing the influence of the different anions. And the influence of a specific anion should be the same in every case and should depend on the atomic numbers of the constituent ions. In short, a series of salts such as the alkali halides should be capable of the same sort of treatment as the elements in Figs. 1 and 2. To test this conclusion we may make use of the data for the alkali halides, which are presented in Table IV. In Fig. 3 we have such a graph, where the values for the chlorides of the alkali metals have been used as the determinant points for the abscissa. The agreement, as can be seen, is all that the experimental data warrants. We may therefore assume that the same rule which was shown to hold for the metals is likewise valid for salts. It should be mentioned, however, in passing, that the above relationship is analogous to one for the molecular volumes which was first pointed out by Fajans and Grimm[1]. Moreover, these are not isolated cases, for the author[2] has already listed eight separate properties of the alkali halide salts which all exhibit the same regularity. No doubt the elucidation of one of these relationships will help in the understanding of the others.

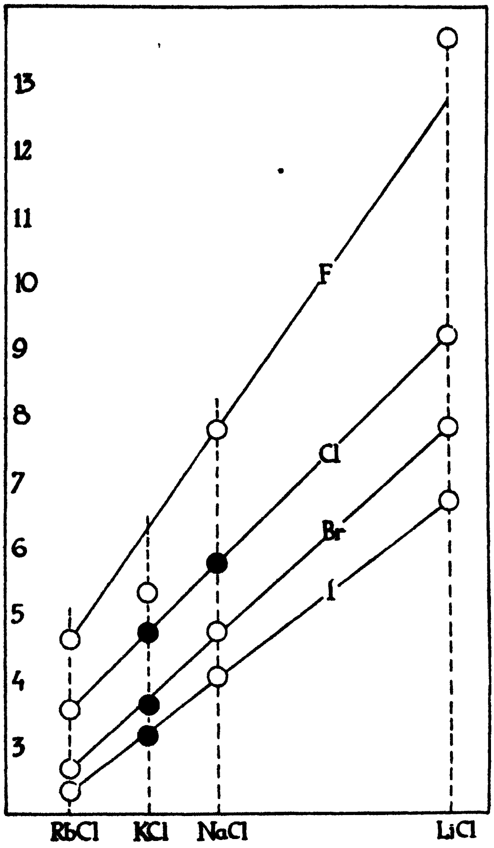


FIG. 3
Frequencies of the Alkali Halides plotted against Frequencies of the Alkali Chlorides.

We may now proceed a step further in our inquiry concerning the nature of the forces which control the behavior of ions in the crystal lattice. We have the expression

$$\nu = 1/2\pi\sqrt{k/m} \qquad (5)$$

where k is the constraint on the ion and m its mass. It is the constraint factor that is of chief importance to this discussion. By definition the constraint is a restoring force per unit displacement and thus provides a measure of the resistance to the displacement of an ion. Obviously it is characteristic of a solid and we may postulate at the outset that the constraint is the resultant of two forces, the attractive and the repellent. Let us analyze this term qualitatively from the standpoint of modern atomic theory. We find that it is one of the canons of this theory that the internal structure of atoms up to the periphery is regulated exclusively by the positive nuclear charge, the atomic number. Positive ions, therefore, formed by the loss of peripheral electrons, may be considered to have dimensions dependent on the atomic number. It is not meant that ions have a definite volume; rather, this term is intended to suggest a limit to the domain of the ion. In a word, it is the realm where the repellent forces, the non-electrostatic forces, come into play; and therefore this repellent force may be considered to be related to the atomic number. On the same grounds we may believe the residual or external field, that is, the attractive force of ions, to be similarly related to the atomic number. But with an ion, the external action is also dependent on the number of electrons lost by the original, neutral atom; and consequently, since periodicity is a function of the number of electrons in the outer shell, we should expect the external field to exhibit distinct periodic changes, and at the same time to vary regularly with the atomic number. Hence, if our general premise is correct, that the constraint is to some extent at any rate a measure of the resultant of the two forces, attractive and repellent, we may then expect the controlling factors of this property to be the atomic numbers of the ions in the lattice.

---

[1] Fajans and Grimm: Z. Physik., 2, 299 (1920).
[2] Scott: J. Phys. Chem., 29, 304 (1925).

Thus, qualitatively at least, we find that atomic theory confirms the fact already mentioned, namely, that the frequency is related to the atomic numbers and valence electrons of the ions in the lattice. There is another aspect of the question which may be of assistance. The nearest distance to which point centers of two ions in a salt, say, can approach will be determined by the two forces under consideration. In short, on the basis of our postulate we may further assume that the distance between the point centers is in some way related to the constraint factor. To anticipate our results we may state that the distance between ions varies in some manner as the square-root of the constraint. Now, in a previous communication the author has presented an empirical rule which expresses the relationship between the lattice distance (nearest approach of ions) and the atomic numbers to an apparently quantitative degree. It is:

$$d_o = a \ln(Z_c - Z_a) + b. \qquad (6)$$

where d_o is the shortest distance between the point centers of ions in a crystal lattice; $(Z_c - Z_a)$ represents the absolute value of the difference of the atomic numbers of cation and anion; and *a* and *b* are constants. In the case of elements it was shown that equation (6) may be written in the form:

$$d_o = a \ln(Z + e) + b. \qquad (6a)$$

where all the symbols have the same significance except e, which equals the maximum number of valence electrons.

Consequently, if the foregoing analysis is correct, we should be able to express the constraint by a similar function, wherein the constants will probably differ because we have no means of knowing the relationship between d_o and the constraint. Furthermore, it will be helpful to make an explanation regarding the constants, a and b. From all that has been said previously one would expect the constants to be characteristic of each group or period. However, recent studies by Bohr indicate that in the case of elements which follow argon the additional electrons fill up the vacant places in the inner orbit instead of going into the outermost orbit. Such a change in the normal sequence must naturally produce a discontinuity or break in the regular variation of properties dependent on the atomic number and valence electrons; and consequently, we must expect this divergence from the normal rule on the part of the electrons to appear in a presentation of equations (6) and (6a) in the periods following argon. Incidentally, it was this abnormal performance of electrons which was alluded to in the discussion of the irregular behavior of the scandium point in Fig. 2. We shall meet with this feature again.

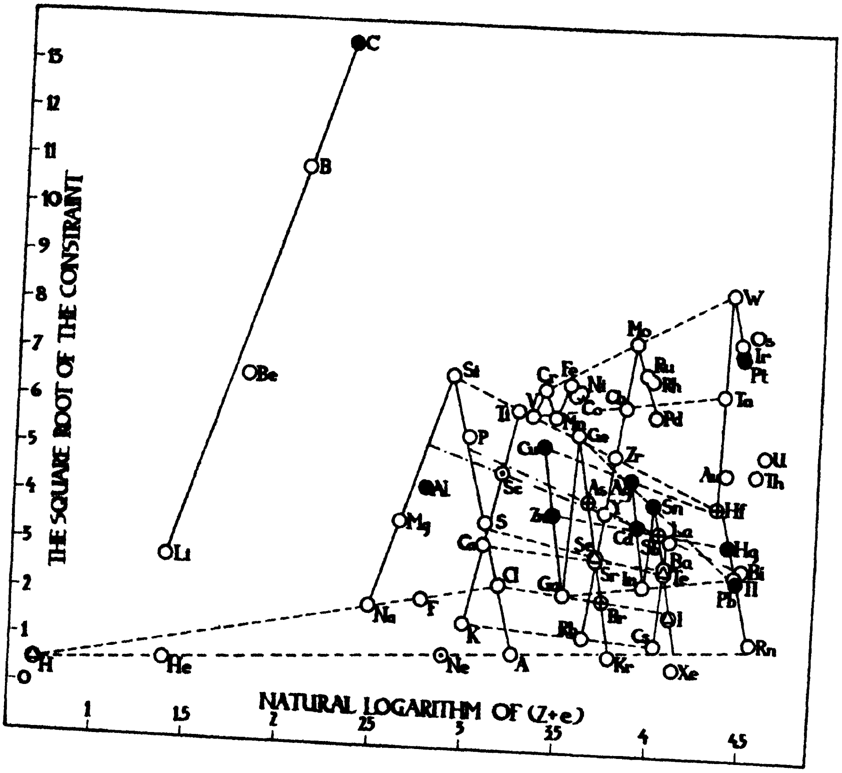


FIG. 4
Periodic Variation of the Square Root of the Constraint of the Elements.

The above discussion may now be summarized by means of an equation:

$$k^{\frac{1}{2}} = 2\pi m^{\frac{1}{2}}\nu = a \ln(Z_c - Z_a) + b. \qquad (7)$$

In the accompanying diagram, Fig. 4, we have the square root of the constraint, $k^{\frac{1}{2}}$, plotted against the function of the atomic numbers, thus depicting the above relationship. All the data essential to the construction of this figure are given in Table II. In a few cases the thermal values for ν have been used and these points are indicated as formerly by black dots. In plotting the graph it was found desirable to divide the values of the constraint by ten. An inspection will show, however, that the values thus plotted are of approximately the same magnitude as the frequencies themselves; that, in fact, the diagram is really a representation, in relative terms to be sure, of the frequencies; and that, finally, the above procedure makes the errors in the "constraint" data of about the same magnitude as in the frequency data, being slightly diminished for the lighter elements and somewhat increased for the heavier elements.

Fig. 4 offers a new means of portraying the variation of the atomic forces, and hence also of the frequency, with the atomic number. We find here a confirmation of the conclusions which were drawn from an examination of Figs. 1 and 2, that the elements of the first period exhibit a normal variation with each other but show a distinct divergence from a normal behavior in relation to the elements of their respective groups. With the remainder of the elements we have a definite variation within each group and period. The representation of the elements of the eighth group is not very significant, first because of the uncertainty regarding the data, and second because of the arbitrary choice of eight for the number of valence electrons. Apart from these elements, the only outstanding defect is that of aluminium, which has already been mentioned in connection with Figs. 1 and 2. Lines for the third group and the fifth sub-group have been drawn arbitrarily, the circles with crosses indicating where the various points might be expected to come according to the abscissa function.

The general agreement of the data is excellent and may be taken as evidence of the fact that we have here a quantitative expression relating the atomic forces and the atomic numbers. Nothing can be stated at this time regarding the constants involved. Nor is it advisable to discuss the many interrelations or the interpretation of the data from a chemical viewpoint. These speculations the author hopes to make up in a subsequent communication.

It remains now to treat the salts in the same way, to see whether they follow the same principle as the elements. This has been done for the alkali halides and is shown in Fig. 5, where we have the square root of the constraint of the different salts plotted against the atomic number function. All of the necessary data are to be found in Table IV. Superficially this diagram appears to be extremely unsatisfactory, a situation which results from the patent uncertainties in the data. Yet, it has been included because, when studied in the light of the information afforded by Fig. 3, there are rather obvious regularities some of which have been indicated by the scheme of the drawing. Instead of going into this matter in detail, a procedure which would be scarcely justified by the flimsy nature of the evidence, we may summarize the probable character of the regularities briefly by stating that they are similar in every respect to those which the author has already enumerated and discussed for the case of the lattice distance.

In conclusion therefore, we may assume that the same principle applies to all polar compounds alike; that the forces which bind ions together in a lattice are controlled by the atomic numbers, the proper function of which is possibly the one that has been discussed in this paper. If this is so, we then have a means of understanding the many relationships that have been pointed out from time to time between the physical properties of metals and salts, for many of these properties are directly connected to the forces existing between ions in a lattice. Moreover, it should be possible to derive quantitative expressions for the relationships between these same properties and the atomic numbers. Finally, if we may believe that the forces which bind ions together are the same forces which hold the valence electrons in an atom, we have a new and definite way of studying the chemical properties of elements and salts.

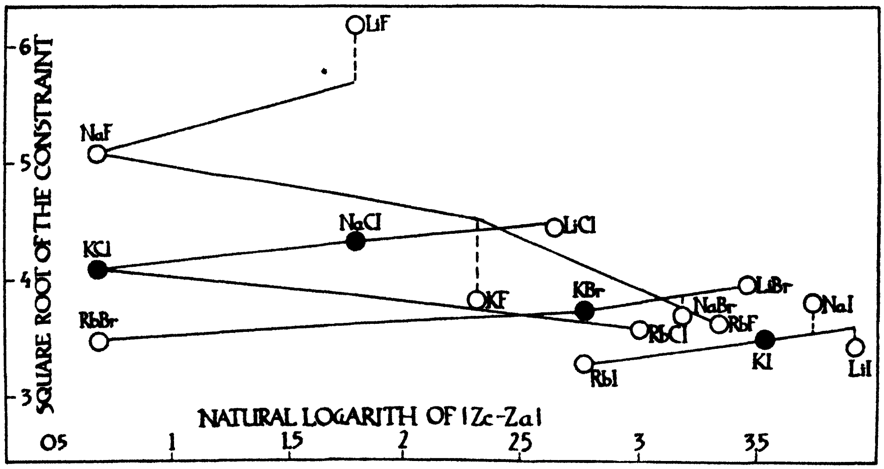


Fig. 5

Variation of the Square Root of the Constraint for a Series of Halide Salts of the Alkali Metals with the Function ln|Zc-Za|.

Summary

The present paper is to be regarded as a continuation of a previous attempt to establish a quantitative relationship between atomic numbers and the properties of ions. Attention is directed chiefly to a study of the forces existing between ions in a crystal lattice. The constraint is taken as a measure of these forces. It is shown how the square root of the constraint of both pure elements and salts may be expressed with certain qualifications by a linear equation involving the natural logarithm of the absolute difference of the atomic numbers of the ions in a crystal. Some relationships between the con-

straint and the physical properties of solids are suggested, a condition which should make it possible to express these same properties in terms of the above function. Furthermore, it is indicated how this empirical relationship may be applied to the chemical properties of ions in metals and salts.

In order to supply the needs of the present study it was necessary to calculate the characteristic frequencies of the elements and salts. These data based so far as possible on recent crystallographic information are presented for about seventy elements and also the alkali halides.

A LABORATORY STUDY OF NITROGEN FIXATION IN THE HIGH TENSION ARC*

BY HERMAN V. TARTAR AND MELVILLE F. PERKINS[1]

Because of the interest in the utilization of cheap hydroelectric power in the Northwest for the fixation of atmospheric nitrogen by the arc process, some experimental work has been carried on in this laboratory. A portion of the results are presented herein and deal mainly with (1) the effect of pressure on the yield of fixed nitrogen, (2) the equilibria obtained with various mixtures of nitrogen and oxygen and (3) the effect of moisture on the yield when air is used.

An extensive review of the literature on the fixation of nitrogen need not be given here. Investigations on the effect of pressure on the oxidation of nitrogen by means of the alternating current arc are not numerous.[2] Practically no quantitative data have been reported on the effect of reduced pressure of this type of arc operating with *good energy efficiency* (shown by yield of fixed nitrogen) at atmospheric pressure. For long the question has been in the minds of investigators as to whether the reaction between nitrogen and oxygen as obtained from the electric arc may be represented as typical reversible reactions conforming to the law of mass action[3]. Published data are not available giving the results of properly determined equilibria using different mixtures of nitrogen and oxygen with arcs operating under conditions necessary for a good yield of fixed nitrogen. Lastly, the literature dealing with the effect of moisture on the oxidation of nitrogen in air by means of the electrical discharge, is both meagre and conflicting[4]. In fact, no extensive quantitative data are available.

Description of Apparatus

(a) *Electrical Equipment*

The power available was a 110 volt, 60 cycle, alternating current. An air-cooled, closed-core transformer of three and one-half kilowatts capacity, was used to give the high tension current. The transformer was calibrated for both resistance and core losses. An adjustable reactance was used to stabilize the arc and control the electrical conditions.

---

* Contribution from the Chemistry Department of the University of Washington.

[1] Du Pont Fellow in Chemistry at the University of Washington, 1921-1923.

[2] Haber et al: Z. Elektrochem., **13**, 725 (1907); **14**, 689 (1908); **16**, 789, 796 (1910); Briner and Naville: Helv. chim. acta, **2**, 348 (1919); J. Chim. phys., **17**, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920).

[3] See Knox: "Fixation of Atmospheric Nitrogen", pp. 7-36 (1921) for review of literature prior to 1920; Steinmetz: Chem. & Met. Eng., **22**, 299, 353, 411 (1920); Daniels, Keene and Manning: Trans. Am. Electrochem. Soc., **44**, 247 (1923).

[4] Warburg and Leithäuser: Ann. Physik, (4) **20**, 743 (1906); Sapozlinikov, Guidima and Kotovi: J. Russ. Phys. Chim. Soc. **45**, 1076 (1913); Briner and Naville: J. Chim. phys. **17**, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920); Gros: Compt. rend. **170**, 811 (1920); Report on the Fixation and Utilization of Nitrogen, p. 137, Bulletin 2041, U. S. War Dept. (1922).

A voltmeter, ammeter, and wattmeter connected in the primary circuit gave the power input and also the power factor. In the secondary circuit the potential across the arc was indicated with a Kelvin electrostatic voltmeter and the current with a milliammeter.

There was some inaccuracy in the smaller readings on the scale of the electrostatic voltmeter and consequently the voltage (used in evaluating yields) across the arc was calculated from the milliammeter readings, the power factor and the net wattage obtained by deducting the transformer loss from the total wattage indicated by the wattmeter in the primary circuit.

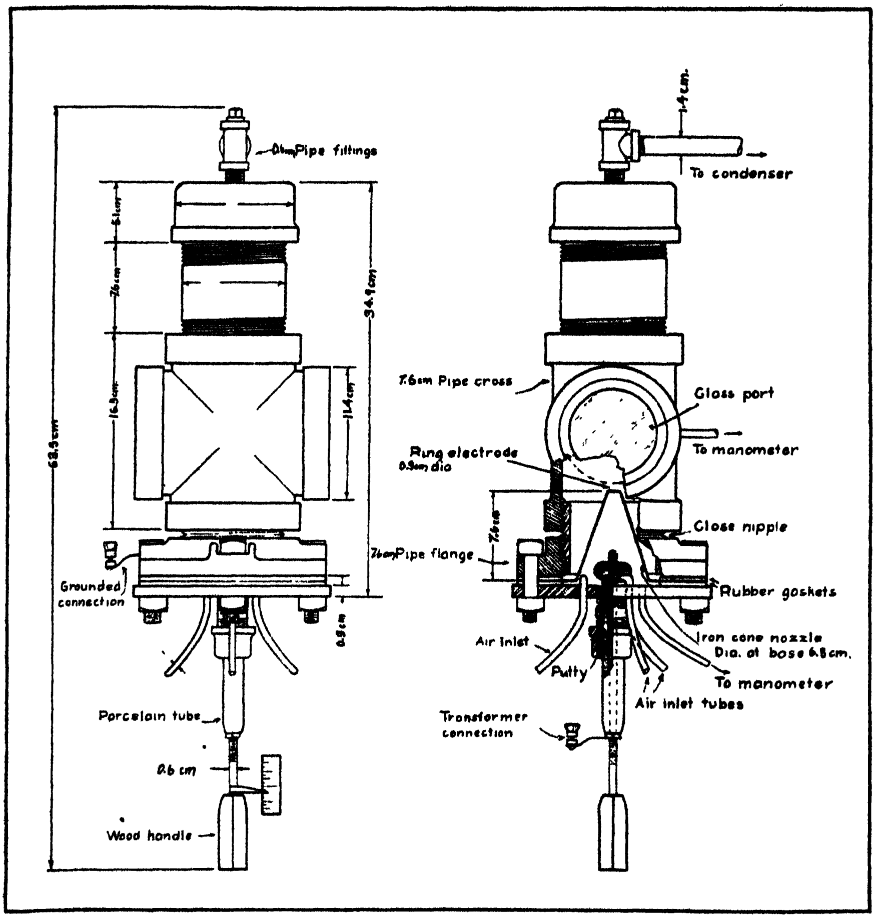


FIG. 1
Arc Furnace

(b) *The Arc Furnace*

The arc furnace shown diagrammatically in Fig. 1 was selected because it gave a good yield of fixed nitrogen. The essential parts were an upper electrode (which was grounded) shaped like a hollow frustrum of a cone, a lower centrally located rod electrode and gas inlet pipes. The gas entered through these pipes at a point slightly above the base and was forced with a whirling motion through the upper electrode. This motion of the gases spread the arc flame and also brought the cold air in very close contact with it; in fact, the arc, thus produced, might be regarded as somewhat similar to that of the Schönherr furnace. The central rod electrode was provided with a screw thread to permit the adjustment of the distance between the electrodes. The furnace enclosure was made largely from 7.6 cm. (3 inch) standard iron pipe fittings and could easily be taken apart. The upper electrode was fastened on a collar and this bolted between the flanges, see Fig. 1. The lower rod electrode was insulated from the remainder of the furnace by means of a porcelain tube set in stiff putty in a pipe bushing which was screwed into the base plate. The gas inlet pipes were 0.63 cm. (1/4 inch) copper tubes fitted tightly into the base plate. They were spaced 120° apart and were equally distant from the central electrode. The gas was given a rapid whirling motion by the nozzle-shaped ends of the inlet tubes which directed the flow tangentially against the frustrum-shaped electrode. A glass window in the side of the furnace permitted observation of the upper part of the arc at all times. Two other openings in the furnace allowed the necessary connections with pressure mannometers to give the gas pressure below and above the upper electrode.

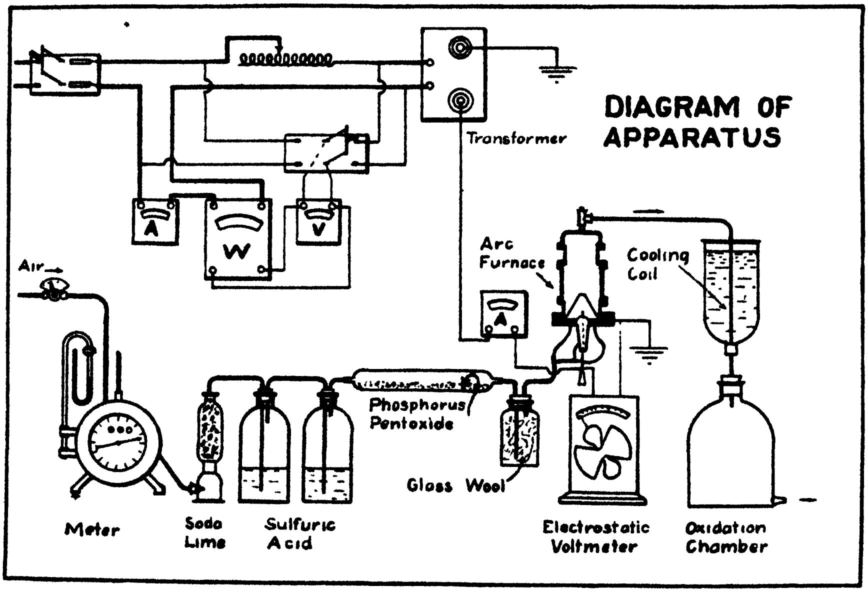


FIG. 2

This laboratory arc furnace gives under proper conditions, an efficiency of 58 grams of fixed nitrogen (as HNO_3) per kilowatt hour, an efficiency near that obtained in commercial practice.

(c) *The Gas Apparatus*

The gas apparatus served two functions: first, to condition and measure the gas before it reached the arc; and second, to absorb the products formed by the action of the arc. Most of the gases were supplied from tanks under considerable pressure, needle valves being used to regulate the flow. The mixtures of nitrogen and oxygen were measured by passing them through the usual wet type of gas meter. The corrosive gases were passed through an all-glass flow meter to determine the volume. When necessary, moisture was removed from the gas by passing it first through concentrated sulfuric acid and then over phosphorus pentoxide.

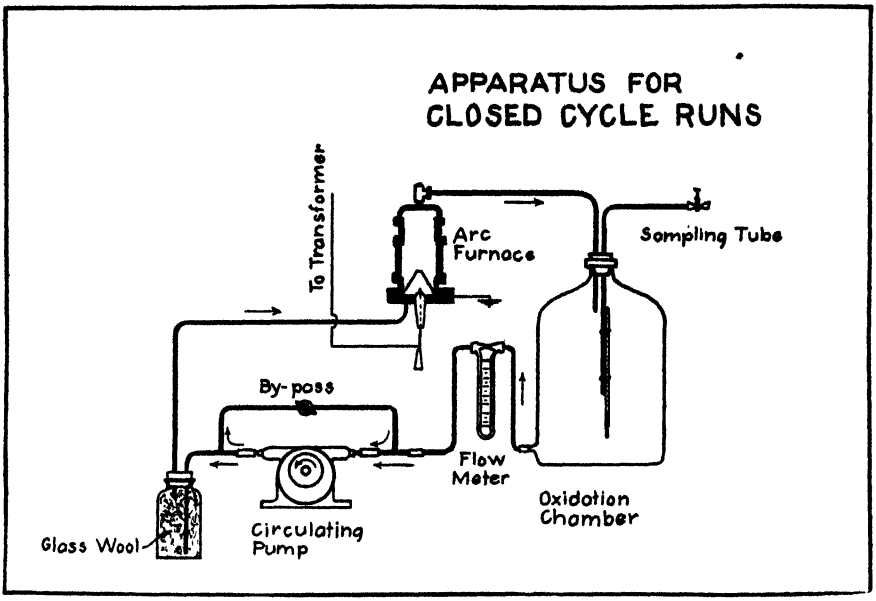


FIG. 3

After leaving the arc, the gas was conducted through a water-cooled glass condenser and then into a five-liter aspirator bottle (hereafter designated as the *oxidation* chamber) in which a considerable portion of the cooled nitric oxide was oxidized to nitrogen peroxide.

The general arrangement of the electrical equipment, furnace, and gas apparatus is shown in Fig. 2.

The apparatus just described was used when the gas was passed but once through the arc, a procedure which is here designated as a *direct run.* In other experiments, the gas was confined in a closed system and circulated repeatedly through the arc, here designated as a *closed cycle run.* A 15-liter bottle served as a gas reservoir and was connected in a closed circuit with the arc furnace, the flow meter and a small "Cenco" positive-acting rotary pump. The pump was equipped with a by-pass or shunt. See Fig. 3. By varying the rate of flow of the gas through the by-pass the desired velocity of the gas through the closed cycle was easily controlled.

(d) *Methods of Analysis.*

The gas leaving the oxidation chamber was sampled in one or more different ways, namely: by vacuum flasks or by an absorption train. The vacuum flasks were round-bottom pyrex flasks, some 500 cc. and some 2000 cc. capacity, with narrow necks fitted with carefully ground stop-cocks. The oxides of nitrogen in the sample were absorbed in an excess of tenth-normal, carbonate-free sodium hydroxide. The excess of alkali was titrated to neutrality with standard acid using para-nitrophenol as an indicator. This procedure was checked against that used by the U. S. Government[1] at Nitrate Plant No. 1, and by the Devarda reduction method.

The absorption train consisted of 6 hydrometer jars 5 cm. wide and 50 cm. long each fitted with inlet and outlet tubes and connected in series with the oxidation chamber. The jars contained a known amount of standard alkali mixed with hydrogen peroxide solution (3%). Glass wool was placed in the jars to break the gas into small bubbles and thus bring about complete absorption of the oxides of nitrogen. At the end of a run the excess of alkali was titrated with standard sulfuric acid using methyl red as the indicator.

When the absorption train was used to evaluate the fixation of reduced pressure runs, a "Cenco" rotary pump was placed in the gas line as a "booster pump" just ahead of the absorption towers so that absorption could take place under atmospheric pressure.

The results obtained using the vacuum flasks and the absorption train were concordant.

Effect of Velocity of Gas through the Arc upon the Yield

In starting experimental work on the formation of nitric oxide with an arc furnace, a determination must be made of the influence of the velocity of air through the arc upon the per cent by volume of nitric oxide and the yield per kilowatt hour. In this investigation, the work was extended to include the mixtures of nitrogen and oxygen varying from the ratio found in air to that of "invert air" (4 vols. oxygen to 1 vol. nitrogen). The composition of gas for each experiment was checked by the analysis of a composite sample extending over the entire run.

The relation between the velocity of air and the electrical values and yield is shown by the data in Table I, also by Fig. 4. The almost constant amperage is due to the reactance in the circuit.

An inspection of Table I and Fig. 4 shows that with constant current and distance between the electrodes, the concentration of nitric oxide for any given mixture decreased with the velocity; and within the limits tried, 200 to 600 liters per hour, the concentration of nitric oxide was a linear function of the velocity.

---

[1] J. Ind. Eng. Chem., **11,** 745 (1919).

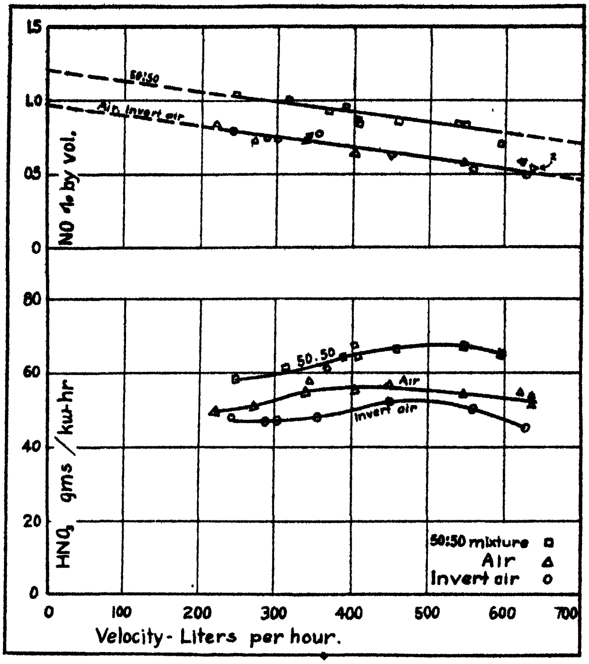


FIG. 4 (upper part)

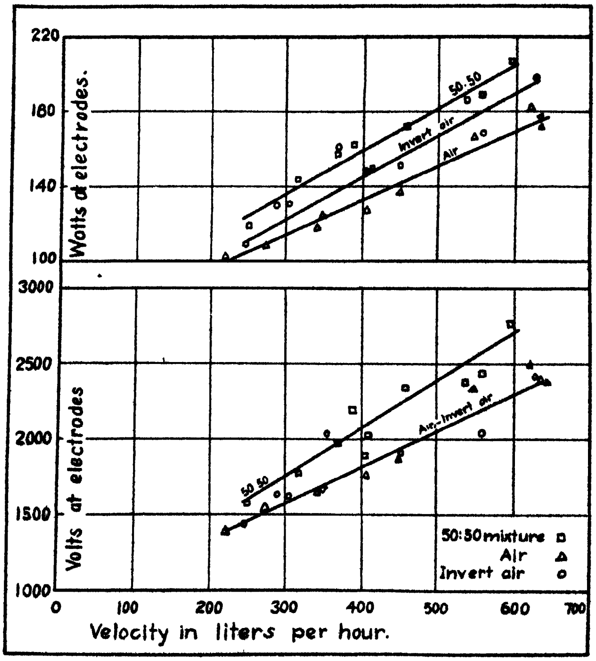


FIG. 4 (lower part)

FIG. 4. (2 parts—upper and lower). Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas thru Arc, 200 to 600 Liters per Hour.

The yield of fixed nitrogen reached a maximum value at an intermediate velocity which depends somewhat on the composition of the gas and its rate of flow. The maximum yields occurred at velocities varying from 350 to 500 liters per hour; or 2000 to 3000 liters per kilowatt hour. These yields at these velocities could be secured only with a current of 90 milliamperes. Doubling the current gave an increase in the concentration of nitric oxide but a decrease in the yield per kilowatt hour. Several runs were made using a current of 30 milliamperes with various gas mixtures at a velocity of approximately 340 liters per hour. The results are recorded in Table II.

TABLE I

Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas, 200 to 600 Liters per Hour

	At electrodes								
Expt. No.	Current milli-amperes	Approximate voltage	Watts, corrected for transformer losses	Velocity of gas thru arc. Liters per hr. Stand. cond.	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen, per cent by volume	Nitric acid (HNO_3) gms per kw.-hr.	Watt-hours required as heat of formation of nitric oxide
Air									
64f	95	1410	104	220	0.84	air	air	50.0	2.06
64g	92	1550	109	273	0.73	”	”	51.5	2.23
64h	92	1660	119	339	0.72	”	”	56.0	2.65
64e	94	1680	125	342	0.76	”	”	58.6	2.91
75	95	1710	128	352	0.72	”	”	56.0	2.84
64i	93	1780	127	404	0.63	”	”	56.0	2.82
64j	93	1880	137	448	0.62	”	”	57.3	3.12
64k	90	2340	167	546	0.59	”	”	54.4	3.61
64n	90	2500	182	622	0.57	”	”	55.5	4.01
64l	89	2400	172	632	0.52	”	”	54.4	3.71
64m	89	2400	177	634	0.52	”	”	52.1	3.67
Approx. 50% N_2. 50% O_2									
66	92	1590	120	241	1.05	43.48	55.47	59.0	2.81
64	95	1790	144	314	1.00	49.50	49.50	61.8	3.54
63	94	1980	158	371	0.93	44.03	55.04	61.4	3.85
64b′	90	2200	163	390	0.96	48.72	50.32	64.7	4.18
64c	93	1900	148	404	0.87	45.76	53.37	67.0	3.93
64b	90	2020	150	407	0.84	48.18	50.98	64.0	3.81
64c′	89	2340	172	461	0.87	48.07	51.06	65.8	4.48
65	93	2380	187	535	0.84	39.58	59.58	67.5	5.02
67	91	2450	189	546	0.83	49.59	49.58	67.2	5.05
68	89	2780	208	593	0.70	49.65	49.65	65.6	5.42
Invert Air									
69	93	1430	110	240	0.80	78.60	20.60	48.7	2.13
70	93	1640	130	289	0.75	79.23	20.02	47.2	2.44
73	94	1630	132	302	0.74	73.63	25.63	47.4	2.48
73b	91	2040	162	357	0.78	78.61	20.61	48.5	3.10
71	94	1910	151	450	0.63	76.68	22.69	53.2	3.19
72	96	2050	169	561	0.54	78.73	20.73	50.6	3.40
74	92	2420	199	628	0.52	78.74	20.52	45.8	3.63

TABLE II

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Atmospheric Pressure: Current 30 Milliamperes: Gas Velocity 340 Liters per Hour

	At electrodes							
Expt. No.	Current milli-amperes	Approximate voltage	Watts corrected for transformer I^2R loss only	Velocity of gas thru arc. Liters per hour. Stand. cond.	Nitric oxide per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	Gms. Nitric Acid (HNO_3) per kw.-hr. (Approximate)
Air								
121	30	2400+	80	351	0.28	Air	Air	35
126	30		80	344	0.28	"	"	34
126′	30		80	344	0.32	"	"	39
Approx. 50% O_2, 50% N_2								
122	30	2400+	80	328	0.33	49.0	50.7	38
Invert Air								
123	30	2400+	80	302	0.13	79.6	20.3	14
124	30		80	322	0.09	81.5	18.4	10
125	30		80	336	0.14	77.5	22.4	16
127	30		80	344	0.11	77.0	22.9	13
127′	30		80	344	0.15	77.0	22.8	18

The data of Table I (and Fig. 4) also show that air and invert air gave the same concentration of nitric oxide at the corresponding velocities. Furthermore, under similar conditions, the 50-50 mixture gave the greatest concentration of nitric oxide. The *relative increase* in the nitric oxide content due to oxygen enrichment depended upon the velocity of the gas at which the comparison was made. At 230 liters per hour there was a gain of 25 per cent; at 550 liters the gain was 40 per cent. This effect of velocity suggests an explanation for the discordant results reported by various investigators for the increase in nitric oxide content resulting from oxygen enrichment of the gas supplied to an arc. An idea of the wide divergence of these results may be obtained from the following quotation from Norton[1]: "McDougal and Howles, in 1900, when using a small experimental plant, nearly doubled the actual yield of NO by changing from air to the mixture of equal volumes, and obtained a concentration of 8.5 per cent NO in the cool gases. The fact of a very pronounced increase in the yield is confirmed by Lepel, by Kowalski and Moscicki (who secured an increase of 50 per cent), by Briner and Durand (37 per cent), by Le Blanc and Muranen (29 per cent), and by Guye (16 to 60 per cent)."

The data (Table I) on the yields per kilowatt hour for air and the 50:50 mixture, show that the enrichment with oxygen, gave an increase varying from 14 to 25%, the latter figure being for a velocity of 600 liters per hour. A comparison of the yields with the 50:50 mixture and with invert air shows a gain varying from 21 to 32%. The maximum increases in yield from the use of the 50:50 gas are in general accord with the mass action law. Fig. 4

---

[1] Norton: Bulletin No. 52, Special Agent Series, U. S. Dept. of Commerce and Labor, p. 84.

brings out the fact that the wattage of the arc was not kept uniform for the different mixtures at any one velocity and consequently close comparisons with respect to the mass law are hardly permissible.

The appearance of the arc changed gradually as the rate of gas flow was increased. At 225 liters per hour (current of 0.1 to 0.2 amperes), a yellow luminous arc was obtained while at 600 liters per hour the steady, luminous zone almost completely disappeared, a blue sparking arc taking its place.

Direct Runs at Reduced Pressure

In the runs at reduced pressures the arc was operated in practically the same manner as in the direct runs at atmospheric pressure. Two stop-cocks were inserted in the gas line; one immediately before the arc furnace and the second after the exit from the furnace. The tube from the latter stop-cock was connected to a large capacity vacuum pump. The arrangement of the apparatus is shown in Fig. 5.

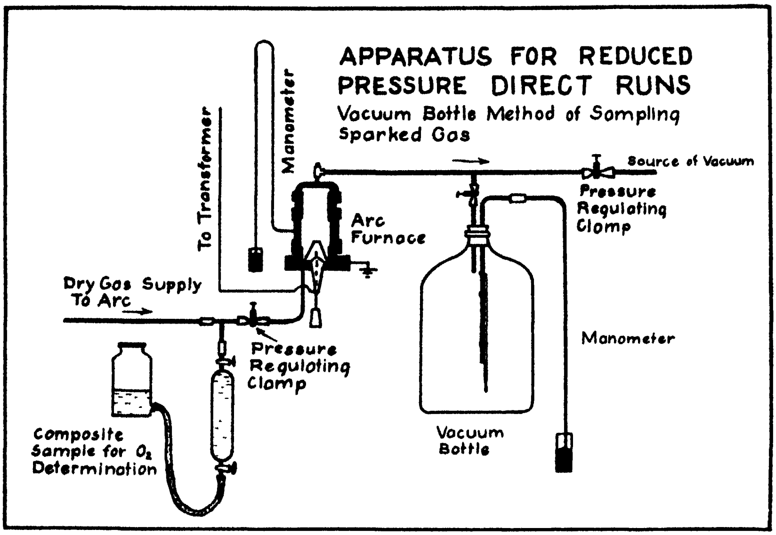

APPARATUS FOR REDUCED PRESSURE DIRECT RUNS
Vacuum Bottle Method of Sampling Sparked Gas
Manometer
To Transformer
Source of Vacuum
Pressure Regulating Clamp
Arc Furnace
Dry Gas Supply To Arc
Pressure Regulating Clamp
Manometer
Composite Sample for O₂ Determination
Vacuum Bottle

FIG. 5

The voltage across the arc decreased with the reduction of pressure. The most noticeable change, however, was in the appearance of the arc itself. Under normal pressure and an air velocity of 340 liters per hour, the arc appeared to be made up of two intermixed parts, one was a bright luminous zone which extended from the rod electrode to about one-half inch above the upper electrode; the other consisted of spark-like streamers that played with a rotary motion between the electrodes. As the pressure was reduced, the luminous zone rapidly disappeared and the spark-like streamers became more numerous, slightly distorted and of a more blue color. The luminous zone disappeared entirely with further reduction in pressure and the arc had the appearance of a spark or brush discharge.

Samples of the gas were taken at the exit of the furnace by the vacuum flask method. Large bottles, 20 liters capacity provided with tightly fitting stoppers with stop-cocks, were substituted for the vacuum flasks previously mentioned.

The experimental data for the reduced pressure runs are reported in Table III and graphically represented in Fig. 6.

TABLE III

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Reduced Pressures

		At Electrode							
Expt. No.	Pressure in arc chamber mm. of Hg.	Current milli-amperes	Approximate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. Liters per hr. stand. cond.	Nitric oxide per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	HNO_3, gms. per kw.-hr.
Air									
92	130	98	800	66	206	0.24	Air	Air	21.6
93	149	96	950	65	219	0.20	"	"	19.0
100	298	96	1120	80	236	0.36	"	"	30.0
86	455	95	1200	85	196	0.62	"	"	39.9
88	451	97	1180	84	201	0.58	"	"	39.0
105	594	93	1170	86	204	0.46	"	"	42.6
64f	768	95	1410	104	221	0.84	"	"	50.0
Approx. 50% O_2, 50% N_2									
96	140	99	900	64	200	0.17	44.92	54.91	15.5
97	147	97	925	62	235	0.20	46.90	52.90	21.8
98	130	96	—	61	203	0.22	48.39	51.39	20.8
99	294	97	1050	76	227	0.38	46.81	52.81	31.5
89	452	94	1150	80	223	0.67	56.67	42.66	53.0
101	460	94	1130	81	245	0.54	48.73	50.73	45.4
104	599	93	1270	101	208	0.41	48.80	50.79	49.7
66	760	92	1590	120	241	1.05	43.48	55.47	59.0
Invert Air									
95	145	97	940	59	239	0.13	76.94	22.94	14.9
91	453	96	1100	85	212	0.60	77.70	21.70	42.2
90	460	96	1125	86	219	0.61	74.69	24.70	43.8
69	772	93	1430	110	250	0.80	78.60	20.60	48.7

The results showed that there was a gradual decrease both in the concentration of the nitric oxide and the yield per kilowatt hour as the pressure was reduced. At corresponding pressures, the 50:50 mixture gave a greater yield than the other mixtures.

An important difference between the direct runs made at atmospheric pressure and those at reduced pressure was the length of time required for the passage of the gas particles through the furnace. For a given gas flow (in these experiments, 200-250 liters per hour), the velocity of the particles through the arc chamber increased with the reduction in pressure. At a pressure of 150 mm., the particles were swept through the furnace at a velocity nearly 5 times greater than when the same quantity of gas was passed through at 760 mm.[1]

The results reported here are of interest in connection with the work of Haber and Köenig[2] with alternating current arcs at pressure around 100 mm.

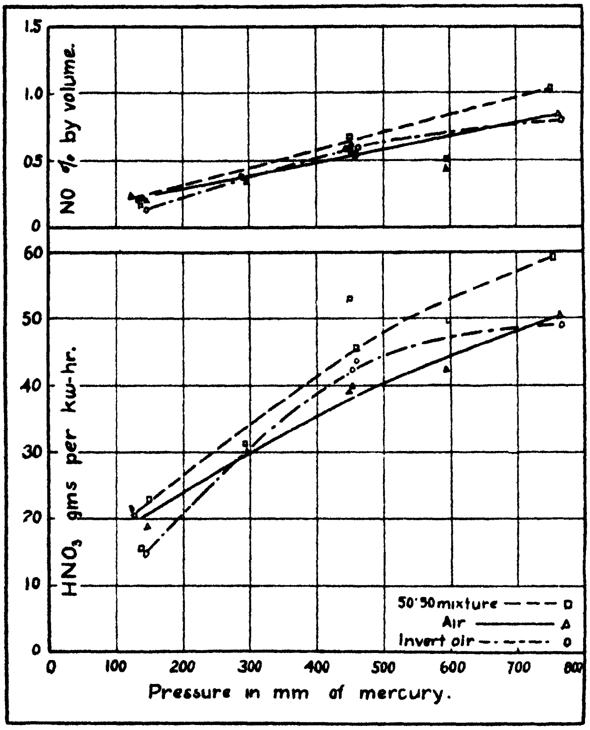


Fig. 6

Direct Runs at Reduced Pressures, (100 to 760 mm.) upon Mixtures of Oxygen and Nitrogen; Gas Velocity 200 liters per hour; Arc Current, 95 milliamperes.

The concentration of nitric oxide obtained depended upon composition of the mixture of nitrogen and oxygen used; 9.8% from air, 14.5% from the 50:50 mixture and 12.5% from "invert air". These high values were obtained, however, with a gas flow of only a few liters per hour. The writers have not obtained any results *indicating that a decrease in pressure may be utilized in securing a greater efficiency in yield by the arc process.*

---

[1] Additional experiments have been made by Mr. P. G. Cohen in this laboratory, reducing the rate of flow of gas through the arc as the pressure was diminished in order to keep the velocity of the particles of gas through the arc constant. The data show that the yield decreased in a manner closely analogous to the results reported above. These additional results will be offered for publication at an early date.

[2] Haber and Köenig: Z. Elektrochem., **13**, 725 (1907).

Closed Cycle Experiments

(a) *The Experimental Part*

The closed cycle runs were made at atmospheric pressure with a power input ranging from 65 to 200 watts. In most cases, the rate of flow of gas was that required to give the maximum yield of fixed nitrogen with air at atmospheric pressure. Closed cycle experiments were conducted on a series of mixtures of nitrogen and oxygen, the content of the latter substance being varied from 20% to 85% by volume. The purpose of these experiments was to determine the equilibrium concentration of nitric oxide obtained by passing the gas repeatedly through the arc. The combined nitrogen existed in the cooler parts of the apparatus largely as nitrogen dioxide. This substance is completely dissociated above 600° into oxygen and nitric oxide. Furthermore, the rate of dissociation is extremely rapid at higher temperatures and consequently the combined nitrogen was assumed to exist as nitric oxide within and in the immediate vicinity of the arc.

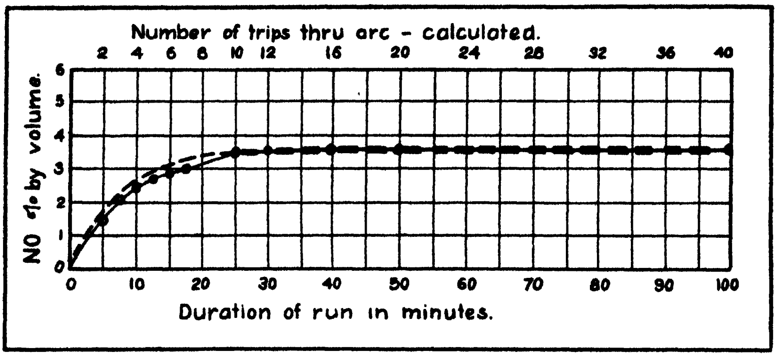


Fig. 7

Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture thrû the Arc at Velocity of 336 Liters per hour; Initial Mixture = Air.

Equilibrium was approached from either direction by obtaining the same final concentration of nitric oxide from mixtures initially containing, on one hand, no nitric oxide and on the other hand, an excess of this substance. The first closed cycle experiments were made to determine the rate of increase or decrease in the concentration of nitric oxide and the time required to reach equilibrium. The change in the nitric oxide content with successive passages through the arc was followed by taking samples at time intervals corresponding to those estimated for the successive cycles. In experiments 61d and 61e, dry air was introduced to replace the gas removed for analysis. This small periodic dilution prolonged somewhat the time required to reach equilibrium. The dilution was reduced to a minimum by admitting the air into the gas line immediately preceding the arc furnace, thus subjecting the newly introduced gas to the action of the arc prior to diffusion. A correction for the dilution was obtained by making a second run under identical conditions without sampling until the arc had been operated for 25 minutes. The results of these experiments are given in Table IV and graphed in Fig. 7, the values corrected for dilution being indicated by the dotted line. In the later runs, dilution attending sampling was avoided by allowing gas of approximately the same concentration to replace that withdrawn. The arc was continued in operation until there was no further change in the concentration of nitric oxide. The extremely slow rate of oxide formation with reduced current strength (30 milliamperes) is shown by the data of experiment 61g also included in Table IV.

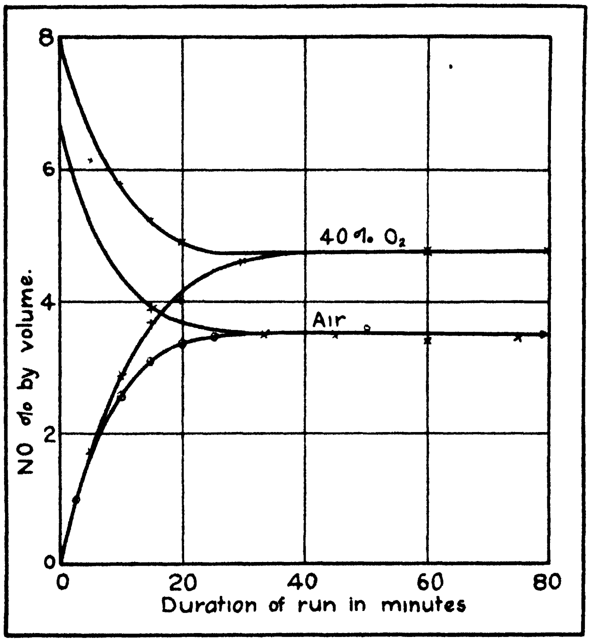


Fig. 8

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions. Velocity of Gas thru Arc, 330 Liters per Hour. Arc Current, 185 milliamperes.

Equilibrium was also approached from both directions using mixtures which had nearer the same total nitrogen and oxygen content; in one case no combined oxide was present, while in the other, the initial nitric oxide concentration was twice the final equilibrium value. Results obtained with mixtures containing different nitrogen-oxygen ratios are given in Table V and represented graphically in Fig. 8. The curves show that the same final concentration of nitric oxide was reached using gases initially free from, or containing an excess of this substance; also, that at a given time, the rate of decomposition was similar to the rate of formation of nitric oxide. Under these conditions, approximately 10 cycles through the arc were required to approach closely the equilibrium value, 80% of the final concentration of nitric oxide being obtained with about 5 cycles.

The next group of experiments were made expressly for the study of the application of the law of mass action to the formation of nitric oxide in the high tension arc. Here the careful determination of the final equilibrium concentrations was the essential factor, the rate of oxide formation being of secondary importance. The equilibrium constant for the reaction, $N_2 + O_2 = 2NO$, was calculated in accordance with the mass action law as follows (concentrations expressed as per cent by volume):

$$K = \frac{(NO)^2}{(N_2) \times (O_2)}$$

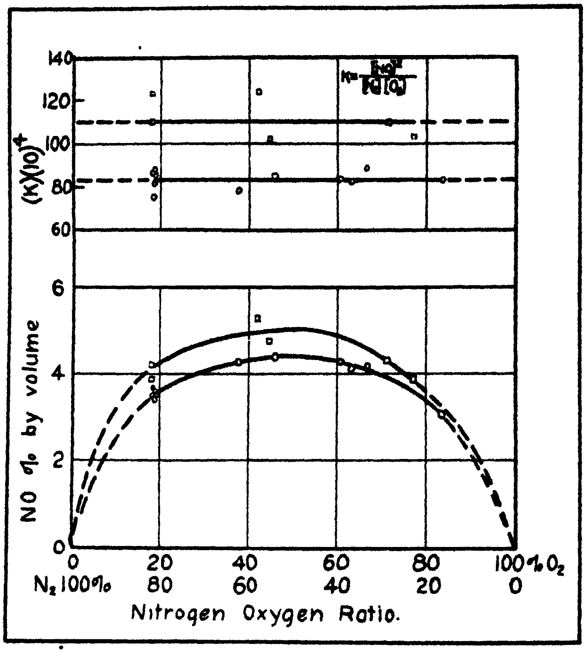


Fig. 9

Equilibria from Closed Cycle Runs.
o = values for arc currents of 100 to 160 milliamperes.
□ = values for arc currents of 30 milliamperes.

These equilibrium runs were made with currents ranging from 30 to 190 milliamperes; the gas mixtures were varied in composition from air to "invert air". The results of these tests are given in Table VI and are shown graphically in Fig. 9. The values obtained for the equilibrium constant K were of the order of (80 to 200) (10^{-4}) and, for convenience, have been multiplied by the factor, 10^4. The values for experiments 51a, 51b, 52a, and 52b were omitted from the graph because a greater gas velocity was used than that necessary for the maximum yield in a direct run. A Thorardson transformer was used to supply the current of 30 milliamperes. The core loss of this transformer was not determined, and consequently the reported wattages are somewhat high. The slow rate of nitric oxide formation with this low current arc greatly prolonged the time required to reach equilibrium.

Table IV

Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture through the Arc

		At electrodes							
Expt. No.	Minutes duration at time of sampling	Current milliamperes	Approximate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.) Liters per hour	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen, per cent by volume	(K) (10^4)
61d	0	190	1240	177	336	0.00			
	2.5	191	1250	185	336	0.97			
	5.0	190	1250	182	336	1.55			
	7.5	191	1260	187	336	2.08			
	10.0	191	1280	188	336	2.44			
	12.5	191	1300	190	336	2.71			
	15.0	190	1300	190	336	2.87			
	17.5	190	1300	192	336	2.96			
	25.0	190	1320	192	336	3.54	19.03	77.43	85.1
61e	0	189	1230	178	336	0.00			
	10	189	1260	183	336		Not sampled		
	20	189	1300	189	336				
	25	188	1310	189	336	3.54			
	30	188	1310	194	336	3.54			
	40	188	1320	194	336	3.67			
	50	188	1350	200	336	3.63			
	100	188	1350	200	336	3.58	19.01	77.41	87.3
61g	0	30	2250	60^{+}	325				
	10	30			325	0.73			
	20	30			325	1.43			
	30	30			325	1.81			
	40	30			325	2.33			
	50	30			325	2.58			
	70	30			325	3.28			
	90	30			325	3.77			
	130	30	2640	65^{+}	325	4.21	18.70	77.10	123.0

$^{+}$Approximate Values.

TABLE V

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions

		At electrodes							
Expt. No.	Minutes duration at time of sampling	Current milli-amperes	Approximate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.)	Nitric oxide, per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	K (10^4)
61e	See Table VII.								
114	0	190	1350	202	335	6.67			
	15	190	1350	202	335	3.92			
	33	188	1340	197	335	3.52			
	45	186	1330	188	335	3.52			
	60	185	1350	193	335	3.44			
	75	188	1320	197	335	3.49			
	90	185	1340	193	335	3.52	17.24	79.24	90.6
115	0	185	1370	192	330	0.00			
	5	184	1400	197	330	1.72			
	10	182	1380	182	330	2.90			
	15	185	1400	199	330	3.72			
	20	185	1440	207	330	4.05			
	30	184	1450	204	330	4.60			
	60	183	1410	197	330	4.78			
	90	183	1410	197	330	4.78			
	100	183	1410	197	330	4.78	35.61	59.61	107.0
116	0	185	1410	199	330	8.02			
	5	185	1410	199	330	6.13			
	10	188	1400	204	330	5.81			
	15	188	1430	209	330	5.21			
	20	188	1430	209	330	4.90			
	30	188	1470	214	330	4.78			
	60	188	1480	219	330	4.78			
	90	188	1480	219	330	4.78	40.61	54.61	103.5

TABLE VI

Closed Cycle Runs at Atmospheric Pressure: Evaluation of Equilibrium Constants

Expt. No.	Minutes duration at time of sampling	At electrodes Current milli-amperes	At electrodes Approximate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.) Liters per hour	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen per cent by volume	$K (10^4)$
	100 to 200 Milliamperes.								
49a	35	100	1500	109	328	3.60	19.00	77.40	88
49b	50	193	1300	145	328	3.48	19.06	77.46	82
51a	30	95	1850	143	634	3.39	19.10	77.50	78
51b	70	193	1500	202	634	3.64	18.98	77.38	90
52a	30	95	1600	114	478	3.54	19.03	77.43	85
52b	50	188	1200	152	478	3.48	19.06	77.46	82
54	30	183	1300	197	340	4.10	63.30	32.60	82
55	20	183	1400	224	331	4.20	61.10	34.70	83
57	30	186	1500	221	334	3.06	83.97	12.97	82
58	30	182	1400	221	334	4.15	66.92	28.93	89
59	40	184	1200	205	331	4.38	46.31	49.30	84
60	25	187	1450	221	331	4.21	38.00	57.80	78
61a	25	187	1350	187	328	3.34	19.13	77.53	75
61d	25	190	1320	192	336	3.54	19.03	77.43	85
61e	50	188	1350	190	336	3.63	18.99	77.38	88
	30 Milliamperes.								
61g	130	30	2640	65^+	325	4.21	18.70	77.10	123
119	90	30	3000	70^+	322	3.86	18.87	77.27	110
117	120	30	2800	75^+	326	5.26	42.20	52.60	124
120	90	30	3000	80^+	324	4.78	44.50	50.70	101
118	120	30	2800	75^+	322	4.32	72.05	23.63	109
128	90	30	2800	80^+	322	3.82	78.03	18.13	103

$^+$Approximate Values.

(b) *Discussion of Closed Cycle Runs*

The rate of oxide formation experiments (Table IV and Fig. 7) afford interesting information concerning the fixation of nitrogen in the high tension arc. The data make possible the numerical calculation of the relative volumes occupied by the spark-like filaments or streamers in which the nitric oxide is formed and by the cooler gas (in the region between the electrodes) surrounding these filaments. The calculation of these relative volumes is based upon the relation of the concentration of the nitric oxide secured by a single passage of the gas through the arc to the concentration of the oxide at equilibrium. The method of calculation is brought out in the following example. In experiment 61d the nitric oxide concentration for the initial passage of air through the arc was 0.97 per cent; the equilibrium concentration, 3.55 per cent. The latter value is the NO concentration of the cooler gas which was in equilibrium with the gas coming from the filament at the particular temperature at which the equilibrium was "frozen". By extrapolation from their experimental data, Nernst, Finckh and Jellinek[1] estimate the temperature corresponding to this concentration to be 3000° Abs.

In the initial passage through the furnace, the gas from the filament (3.55 per cent NO) was diluted with the air from the cooler zones which reduced the concentration of nitric oxide to 0.97 per cent. This means that out of every 100 cc. of gas which passed through the arc, 27.3 cc. passed through the filaments and 72.7 cc. through the adjacent cooler zones. In the second passage each 27.3 cc. of gas from the filaments (3.55 per cent NO) was cooled by mixing with 72.7 cc. of gas containing 0.97 per cent NO producing a concentration of 1.67 per cent NO. In the third exposure to the arc, each 27.7 cc. of 3.55 per cent gas from the filaments was diluted with 72.7 cc. of 1.67 per cent gas producing a concentration of 2.19 per cent NO. The content of nitric oxide for the succeeding passages may be calculated in a similar manner. The calculated and experimental values for the first 11 cycles are given in Table VII.

TABLE VII

Comparison of Observed and Calculated Nitric Oxide Concentrations for Successive Exposures to Arc

Cycle	Per cent NO (calc.)	Per cent NO (observed)	Per cent NO (observed, corrected for dilution attending sampling.)	
1	——	0.97	0.97	
2	1.67	1.55	1.70	
3	2.19	2.08	2.20	
4	2.56	2.44	2.60	
5	2.83	2.71	2.90	
6	3.02	2.87	3.10	
7	3.17	2.98	3.30	
8	3.27	——	3.40	From curve.
9	3.35	——	3.50	
10	3.40	——	3.50	
11	3.44	3.54	3.54	

The calculated nitric oxide content at the successive cycles corresponds with the observed values indicating that the assumptions made are close to the truth.

Upon the basis of the preceding assumptions and calculations an estimate of the energy efficiency for the most effective operation of an arc can be made. The energy required is that necessary to heat the air in arc filament (only) from room temperature to 3000° Abs. plus the heat of formation in the nitric oxide produced. According to Lewis and Randall,[2] the molal specific heat for air, oxygen, nitrogen and nitric oxide, is best represented by the equation:

$$C_p = (6.5 + 0.001T)$$

---

[1] Nernst, Finckh and Jellinek: Z. anorg. Chem., **45**, 116, 126, (1905); **49**, 213, 229 (1906).

[2] Lewis and Randall: J. Am. Chem. Soc., **34**, 1128 (1912).

in which C_p is the molal specific heat in calories at constant pressure and T is the absolute temperature. This equation is based upon experimental data reaching to 2000° Abs.; consequently, its application to higher temperature involves an extrapolation. However, this is the best data available so far as the writers are aware. The calculation of the heat required to heat one mol of air from 293° to 3000° Abs. is made by the integration of the equation $Q = C_p dT$ between the limits corresponding to these temperatures.

$$\begin{aligned} Q &= \int_{293}^{3000} (6.50 + 0.001T)\ dT \\ &= 6.5\ (3000 - 293) + 0.001/2\ (3000^2 - 293^2) \\ &= 22052 \text{ calories.} \end{aligned}$$

In addition to heating the air, 0.0355 mol of nitric oxide is formed. The molal heat of formation of nitric oxide is −21600 cal.; to form 0.0355 mol requires 767 calories. The total heat required is therefore, 22052 + 767 = 22819 calories.

The best efficiency (yield per kw-hr.) secured with the arc used in this investigation was obtained in experiment 64c, previously reported in Table I. The data are as follows: air velocity, 342 liters per hour; arc current 94 milliamperes; power at the electrodes, 125 watts; and the concentration of nitric oxide produced 0.76 per cent. The equilibrium concentration of nitric oxide for these conditions is 3.55 per cent. Using these concentrations as a basis, the calculated air passing through the arc filament is 22.5 per cent of the total air going through the furnace, or 76.95 liters (3.44 mols) per hour. The heat required for the heating of this quantity of air from 293° Abs. to 3000° Abs. is, 3.44 × 22819 = 78497 cal. The actual experimental energy was 125 watt hours, which is equivalent to 107500 calories. Hence, (78497 ÷ 107500) (100) or 73 per cent is the thermal efficiency obtained in this experiment in which the yield was 58 grams of nitric acid per kilowatt hour.

The value of the equilibrium concentration also permits the calculation of the maximum concentration of nitric oxide to be secured by a single passage of the gas through the arc. The velocity of decomposition of nitric oxide has been investigated by Jellinek[1] for the temperature range 689°C. to 1750°C. From this reaction constant and the equilibrium constant for the reaction, the reaction constant for the formation of nitric oxide can be determined. From these data the rates of formation and of decomposition of nitric oxide in any given mixture can be calculated[2]. The calculated time required for the decomposition at 1900° Abs. of 40 per cent of the nitric oxide present in an air mixture at 1 atmosphere containing initially twice the amount of this substance that will be present when equilibrium is established, is 2-1/2 minutes. At 1773° Abs. the time required for this amount of decomposition is 21 minutes. The gas from the arc zone should surely be cooled quickly to at least 1900° Abs. to "freeze" the equilibrium. Below this temperature the rate of decomposition will be sufficiently slow that the gas may be cooled less rapidly without appreciable loss of combined nitrogen. In suddenly chilling the gas from the arc filament from 3000° Abs. to 1900° Abs. the cold air will be heated to 1900° Abs. The amount of heat absorbed in heating one mol of air from 293° Abs. to 1900° Abs. may be estimated as follows:

---

[1] Jellinek: Z. anorg. Chem., **49**, 263 (1906).

[2] For details concerning the formulations and method of calculation, the reader is referred to pp. 134, Bulletin 2041, U. S. War Dept.; Report on the Fixation and Utilization of Nitrogen.

$$\begin{aligned} Q &= \int_{293}^{1900} (6.5 + 0.001T)\,dT \\ &= 6.5\,(1900 - 293) + 0.001/2\,(1900^2 - 293^2) \\ &= 12{,}207 \text{ cal.} \end{aligned}$$

Previous calculations show that 22052 cal. are required to heat 1 mol of air from 293° Abs. to 3000° Abs. Then

$$22052 - 12207 = 9845 \text{ cal.}$$

the heat to be removed in cooling 1 mol of the gas from the arc filament to 1900° Abs. And $9845 \div 12207 = 0.806$, the number of mols of cold air required to cool 1 mol of the gas from the filament. If the gas from the filament contains 3.55 per cent of nitric oxide (the equilibrium value) and is cooled without further decomposition by adding 0.806 mol of cold air, the cooled gas will contain 1.91 per cent of nitric oxide. This is the calculated maximum concentration of this substance that can be secured from an arc with cooling as effective as that accomplished in this investigation. This value closely approximates the maximum concentration of nitric oxide which has been secured in commercial practice with good energy efficiency, viz. 1.8 per cent by the Schönherr-Hesselberger furnace.

The equilibrium concentrations (closed cycle runs) for the different amperage arcs indicated that the "freezing" of the equilibrium by mixing with cold air in the furnace was very effective. From Jellinek's data the estimated time for the decomposition at 3000° Abs. of 40 per cent of the nitric oxide in an air mixture containing 200 per cent of the equilibrium concentration of this substance, is 1.2×10^{-5} seconds. The writers realize that this reaction velocity was obtained by extrapolation from experimental data secured at lower temperatures. Nevertheless, the rapidity with which the equilibrium was "frozen" with this type of whirling arc is almost incredible.

Many cycles were required to secure equilibrium with currents of 30 milliamperes. This indicates that the volume of the gas passing through the filament was small compared to the volume passing through the surrounding cooler zones, being of the order of a fraction of a per cent. The meagre data so far secured hardly justify the calculation of the actual volume of the filament. However, the results show that a reduction in the arc current strength decreases the effective volume of filament. Furthermore, there is no indication that decrease of current is necessarily attended by a change of the average kinetic energy of the particles in the filament.

The closed cycle experiments furnish trustworthy data (see Tables V and VI) concerning the application of the law of mass action to the fixation of atmospheric nitrogen in the high tension arc having good energy efficiency. The curves in Fig. 9 show in each case that the concentration of nitric oxide at equilibrium increases in a regular manner to a maximum value as the volumes of nitrogen and oxygen forming the mixture become equal. Furthermore, the consistent values for the equilibrium constant for a series of experiments at a given current strength are in close accord with the mass action law. The difference in the values of the equilibrium constants for arcs of different current strengths is due to the "freezing" of the equilibrium at different temperatures. The writers have not obtained thus far any evidence with the experiments carried out, of any deviation from the mass action law due to any special "electrical effects".

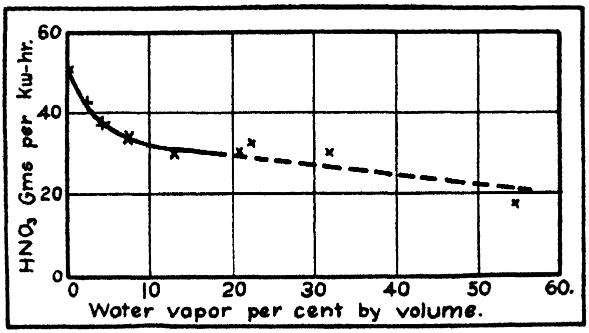


FIG. 10
The Effect of Water Vapor. Direct Runs at Atmospheric Pressure.

The Effect of Water Vapor

In the arc fixation of nitrogen in commercial quantities the oxygen-nitrogen mixture is simply air. Since the atmosphere contains moisture, information regarding its effect on fixation was determined for mixtures of air and water vapor in which the moisture content ranged from 2 to 50% by volume. The results are given in Table VIII and Fig. 10. In this series of experiments the arc furnace was inverted to prevent short-circuiting the high tension electrode due to condensation after passing through the arc of water from mixtures high in moisture.

The values for experiments with a moisture content as high as fifteen per cent are accurate, but the precision is somewhat less in the runs containing a greater amount of water vapor because of a tendency toward premature condensation of the moisture. Ample precautions were taken in the analyses to prevent any loss of fixed nitrogen due to a film of moisture on the walls of the apparatus. In order to carry out the experiments with the greatest precision, the entire furnace should be inclosed in a thermostat at a temperature somewhat above the dew point of the air-water mixture used. The authors have not yet had the opportunity to arrange an apparatus of this sort. Consequently, the experiments made thus far with higher percentages of water vapor may be somewhat in error.

These findings show that even with 2.6% moisture, which corresponds to 100 per cent humidity at 22°C., the yield was reduced to 42.1 grams of nitric acid per kilowatt hour which is a 25% decrease in production. Evidently a small amount of moisture may cause a very appreciable decrease in yield.

Table VIII

The Effect of Water Vapor

Direct Runs at Atmospheric Pressure on Moist Air

Expt. No.	Current Milli-amperes	Approx. voltage	Watts corrected for transformer losses	Velocity of gas thru arc. Liters per hour. (Stand. cond.)	Water vapor per cent by volume	Nitric oxide per cent by volume	Gms. HNO_3 per kw.-hr.
33	96	1740	136	2.6	2.6	0.56	42.1
34	97	1700	136	4.4	4.4	0.49	37.5
35	97	1810	151	7.5	7.5	0.47	33.8
36	96	1810	151	13.7	13.7	0.39	30.7
30	94	1720	129	20.8	20.8	0.34	30.2
29	94	1710	128	21.9	21.9	0.35	32.7
38	96	1680	141	32.0	32.0	——	30.2
39	92	——	153	54.3	54.3	0.136	18.0

Acknowledgment

Grateful acknowledgment is made to the E. I. du Pont de Nemours and Company for the grant of a fellowship which made possible this investigation.

Summary

1. A satisfactory laboratory arc furnace with good energy efficiency has been constructed.

2. A high gas velocity favored a high yield of fixed nitrogen per kilowatt hour but gave a lower per cent by volume of nitric oxide. Excessively high air velocities gave a low output in respect to both yield and concentration of fixed nitrogen.

3. The use of reduced pressure (with a gas velocity suitable for a good yield of fixed nitrogen at atmospheric pressure) gave a decrease both in the concentration of nitric oxide and in yield of fixed nitrogen per kilowatt hour.

4. A study has been made of the equilibria obtained with various mixtures of nitrogen and oxygen using a high tension arc with different amperages. The results show that the mass action law applies to the equilibria obtained. The temperatures at which the equilibria were "frozen" show that the cooling from the whirling arc is very efficient.

5. A method has been given which permits the calculation of the concentration of nitric oxide resulting from repeated exposures of a nitrogen-oxygen mixture to a high tension arc.

6. A value, based upon experimental data, has been given for the theoretical maximum concentration of nitric oxide that may be obtained with an arc, at an energy efficiency equivalent to 60 grams of nitric acid per kilowatt hour, for air supplied at room temperature and atmospheric pressure.

7. The presence of water vapor in the air supplied to the arc reduced both the yield and the concentration of the nitric oxide.

ORGANOGELS OF SILICIC ACID—THE REPLACEMENT OF WATER IN THE HYDROGEL BY ALCOHOL

BY J. B. FIRTH AND W. L. PURSE

Graham[1] showed that various organic liquids were capable of displacing the water of the hydrogel of silicic acid. Thus in the case of alcohol he says of hydrated silicic acid, "the combined water leaves the acid to diffuse into the alcohol and if the alcohol is repeatedly changed the *entire* water is thus removed, alcohol at the same time taking the place of water in combination with the silicic acid. The process is reversed if an alcogel be placed in a considerable volume of water. Such changes illustrate the predominating influence of mass."

Graham's results show that an alcogel prepared and analysed by him contained 383 parts of alcohol to one part of water..

Bachmann[2] showed that the weight of different liquids taken up by silica gel is proportional to their density. Measurements with water, benzene, chloroform, ethyliodide and acetylene tetrabromide gave concordant results.

Neuhausen and Patrick[3] came to the conclusion that it is impossible to remove all the water from the hydrogel of silicic acid by repeated immersions in anhydrous alcohol, acetone or benzene. They state that their results indicate that Graham was in error when he stated that it is possible to replace all the water from a silica hydrogel by other liquids. They are of the opinion that the residual small percentage of water in silica gel is held with a force that exceeds that exhibited between atoms of many stable compounds.

The authors being desirous of preparing, if possible, an alcogel of silicic acid free from water carried out experiments with this object in view, and the results are described in the present communication.

Experimental

Preparation of Gels. The sodium silicate used was specially prepared and was free from iron and gave no indication of carbon dioxide with hydrochloric acid. The composition corresponded to $1Na_2O:2SiO_2$. A solution of density 1.118 was prepared and added to an equal volume of 3N hydrochloric acid.

A series of gels were prepared as follows:—

(a) The acid and silicate solutions were heated to 45° and after mixing, the product maintained at 45° until the gel had set. The resulting gel was then washed with hot distilled water until free from sodium chloride, then dried in a steam oven, heated in an air oven at 320°, again washed with distilled water and finally allowed to dry at room temperature. The resulting gel contained 33 per cent of water.

---

[1] Graham: J. Chem. Soc., **17**, 318 (1864); Pogg. Ann. **123**, 529 (1864).

[2] Z. anorg. Chem., **79**, 202-208 (1913).

[3] J. Am. Chem. Soc., **43**, 1844-6 (1921).

(b) Solutions mixed at 50° and allowed to set at this temperature. The resulting gel was free from sodium chloride and dried at 120°. The resulting gel contained 10.83 per cent of water.

(c) Solutions mixed and gel allowed to set at room temperature. The gel was then washed free from sodium chloride and dried at 100°. The product contained 7.53 per cent of water.

(d) The gel was prepared as in (c) but was dried at 100° without washing out the sodium chloride. A greater portion of the sodium chloride was expressed from the gel during drying.[1]

The resulting product was then washed free from sodium chloride and finally dried at 110°, after which the water content was 14.7 per cent.

Treatment of the Gels with Alcohol

The alcohol used was dried first over pure lime and finally over metallic calcium. The alcogels were prepared by two methods:—

(a) The gel was immersed in the dry alcohol (1 gram of gel to 150 cc of alcohol) at room temperature and allowed to stand for two days, after which the treatment was repeated three times.

(b) A current of dry air was saturated with alcohol vapour and passed over the gel. The gel was contained in a tube of 5 m.m. bore and fitted with two taps. The tube containing the gel was weighed at intervals, the experiment being continued until no change of weight could be detected over a period of three hours, a condition which it usually required three days to attain.

Results

The alcogels obtained by both the above methods were analysed by the usual combustion methods of organic chemistry.

Towards the end of the combustion the boat containing the gel was raised to a bright red heat (above 900°) in order to drive off the last traces of water out of the gel.

From the amounts of carbon dioxide and water formed, the percentage of alcohol and water in the gel were calculated. Typical results obtained are given in Table I.

TABLE I

Method of preparation of gel.	Original% of water.	Dynamic Method. %Alcohol.	%Water	Static Method. %Alcohol.	%Water
a	33.0	32.18	0.73	22.73	9.81
b	10.83	30.92	0.64	25.38	5.12
c	7.53	30.30	0.57	24.25	5.82
d	14.7	29.09	1.11	24.23	7.06

Discussion

From the above results it would appear that the extent of the replacement of water by alcohol in a silicic acid gel is very markedly affected by the method adopted.

---

[1] Cf. Fells and Firth: J. Phys. Chem., **29**, 241-248 (1925).

Within the limits of the experiments described the replacement of the water is much greater by the dynamic method than by the static method.

Although in our experiments we have not been able to reduce the water content to a value as low as that obtained by Graham, we do not regard Graham's result as impossible. The *complete* replacement of the water by alcohol would no doubt, be very difficult to attain and it seems very probable that the removal of the last traces of water would be a very slow process at ordinary temperatures, particularly by the static method.

Certain of our results by the static method are in fair agreement with those of Neuhausen and Patrick (loc. cit.), yet by the dynamic method much more complete replacement has been obtained. Hence we are of the opinion that the limited results of Neuhausen and Patrick do not justify their conclusion that Graham's results are erroneous. Hoffert[1] and others have shown that the sorptive capacity of a silicic acid gel may vary over quite a wide range; the method of preparation, water content, age of the gel and packing density being some of the factors concerned. Again it has been shown by Hoffert (loc. cit.) that the retentivity of the gels, for example in the case of benzene, also varies.

From our results, under the conditions described, it would appear that the retentivity of water varies with the different gels employed. That some of the water is more tenaciously held does not preclude its *ultimate* replacement under the most suitable conditions.

Summary

1. The replacement of water by alcohol of four silicic acid gels prepared under different conditions and of different initial water content have been examined.

2. Within the limits of the experiments, the replacement is more complete by the dynamic method than by the static method.

3. The most complete replacement gave a final water content of 0.57 per cent associated with 30.3 per cent of alcohol; the initial water content being 7.53 per cent.

We desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us (W. L. P.) to take part in this work.

University College,
Nottingham,
England.
Feb. 2 (1926).

---

[1] J. Soc. Chem. Ind., **44**, 360T (1925).

THE REACTIVE NATURE OF ALDEHYDES FROM THE STANDPOINT OF THE APPARENT ELECTROMOTIVE FORCE

BY SAUL B. ARENSON, PLEASANT ERNEST ROLLER AND D. J. BROWN

Haber and Russ[1] were the first to show that for the reversible oxidation and reduction of organic compounds the same factors are involved as for the same type of inorganic reactions. Later work[2] confirms their conclusions for this class of organic compounds. For organic substances that are oxidized or reduced irreversibly, except to show that some of them develop an apparent electromotive force, very little appears in the literature. Baur[3] showed that the alkaline solutions of aldehydes show a large variation in the apparent electromotive force on standing. Stieglitz[4] demonstrated that alkaline solutions of formaldehyde may be used as the negative electrode of a cell to deposit silver from solution at the other electrode apparently reacting the same as a reversible reducing agent. Other alkaline solutions of aldehydes react the same. St. Bugarszky[5] found that the velocity of reduction by aldehydes is inversely proportional to the concentration of the hydrogen ions. While no quantitative measurements are available, apparently the other reactions of aldehydes are affected similarly by the relative concentration of the hydrogen ions.

The following observations were made to secure further information on the relation of the apparent electromotive force to the alkalinity of the solutions and the reactions of aldehydes.

Experimental

Since preliminary experiments indicated that the apparent electrode potentials of the aldehydes were approximately of the same value as the oxygen electrode, all operations from the preparation of the solutions to the final measurement of the electromotive force were made in an atmosphere of nitrogen. This nitrogen was prepared by passing air or commercial nitrogen thru a chain of bottles filled with copper foil in contact with a solution of ammonium chloride and quite concentrated ammonia, then with the ammonia vapor thru a silica tube containing a tightly wound copper gauze heated to 500-600°C. The excess ammonia was removed by passing the nitrogen thru solutions of sulfuric acid.

"Conductivity water" was used to prepare all solutions. The acid solutions were prepared by recrystallizing $H_2SO_4.H_2O$ twice from conductivity water and then diluting. The sodium hydroxide solutions were prepared by dropping metallic sodium into a two-phase mixture of ether and water, the ether was evaporated in vacuo, and the concentrated solution diluted.

---

[1] Haber and Russ: Z. physik. Chem., **47**, 257 (1904).

[2] Clark: Chemical Reviews, **2**, 127 (1925).

[3] Baur: Ber., **34**, 377 (1901).

[4] Stieglitz: Science, **27**, 775 (1907).

[5] St. Bugarszky: Z. physik. Chem., **48**, 63 (1904).

The acetaldehyde was prepared from paraldehyde by the method of McLeod[1]. The temperature of the condenser was maintained at 22° ± 2C. It was collected in an oxygen-free container, which in turn was emptied by pressure into a two-liter flask and diluted with conductivity water at 0°C. The strength of the acetaldehyde solution was determined by the method of Seyewetz and Bardwin[2], in which the aldehyde is titrated in the presence of sodium sulfite with a standard acid.

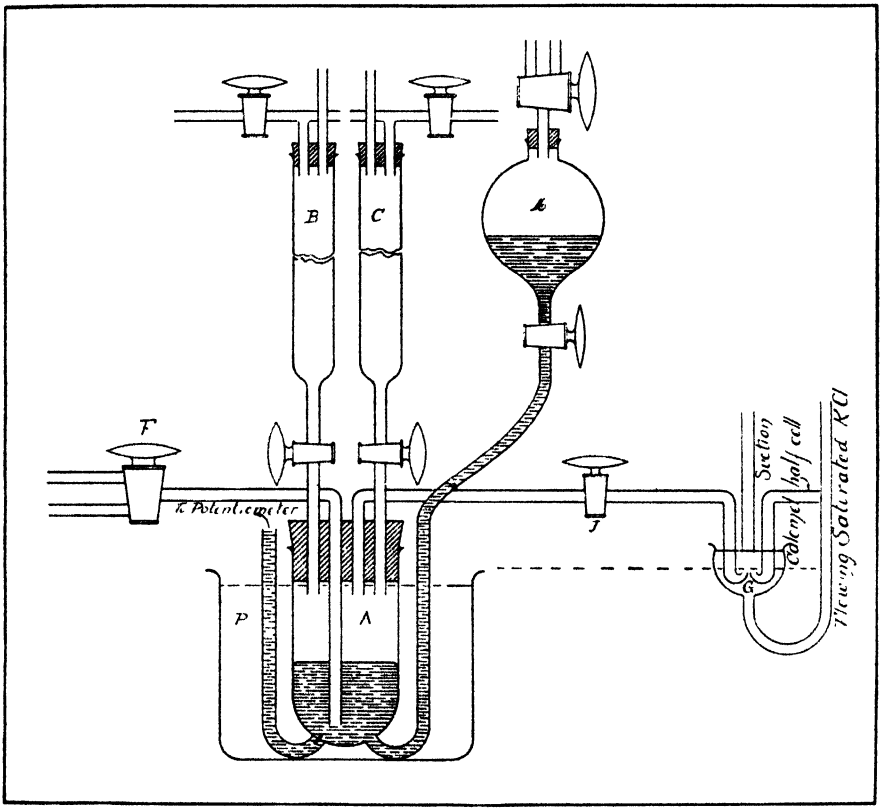


Fig. 1
Aldehyde Half-cell.

Chloral hydrate best grade was recrystallized from carbon bisulfide which had been shaken with lead carbonate and then distilled.

The potentials of the aldehyde half-cell were measured in terms of the calomel electrode by means of a Weston cell, a Leeds and Northrup Type K potentiometer, and Type R galvanometer. Both electrodes were kept in beakers of distilled water which were in a thermostat at 25° ± .05 C. All work except the titrations was done in a room lighted by ruby lights.

---

[1] McLeod: Am. Chem. J., **37**, 20 (1907).

[2] Seyewetz and Bardwin: Bull., **33**, 1000 (1905).

The results were obtained by the use of the container for the aldehyde solutions shown in Fig. 1. Tube P was filled with mercury and sealed at the bottom with a platinum insert to complete the circuit from the mercury within the container to the potentiometer. When an observation was being made, the contents of the electrode chamber was caused to flow slowly into the flowing saturated potassium chloride bridge, G. The procedure was as follows:

Mercury from M was forced into A, the contents of A flowed thru J into G. "Oxygen-free" water was then admitted thru F to A while the surface of the mercury was lowered, J being kept closed. F was closed and the container emptied as stated in the first sentence. After A was completely washed, the balance of the water was removed by admitting nitrogen thru F. By means of nitrogen, solutions kept in thermostats were forced into burets, B and C, and then the measured quantity of each was forced into the electrode chamber, A, and immediately stirred by the nitrogen thru F for several seconds, F was closed and mercury from M was allowed to force sufficient of the solution thru J to make a circuit thru G with the calomel electrode—by rapid manipulation it was found possible to make the first observation of the electromotive force within one minute after the solutions were admitted to the electrode. After each reading J was closed. A little mercury was permitted to enter A before each subsequent reading, thus securing the flow while the reading was being made.

Results

For approximately molar solutions of acetaldehyde and chloral hydrate in normal sodium hydroxide the velocity of change in the observed electromotive force was very large. For this concentration with acetaldehyde the results check those given by Baur[1]. The results with the more dilute solutions of acetaldehyde in sodium hydroxide were as follows:

+ .071 molar acetaldehyde,				.0105 normal sodium hydroxide			
2 min	−.1180	2 min	−.1186	3 min −	.1223	2 min	−.1179
4	.1255	4	.1286	5	.1263	5	.1183
7	.1280	6	.1300	17	.1285	9	.1199
10	.1179	12	.1290	29	.1275	19	.1193
22	.1112	30	.1253	107	.1229	89	.1110
		114	.1245				

The mean minimum results for the concentrations studied were

Acetaldehyde	Sodium hydroxide	E.M.F.
.071 molar	.0105 normal	−.128 volts
.017	.0105	−.113
.0121	.00525	−.092
.0263	.0525	−.155
1.0	1.0	−.239

---

[1] Baur: Ber., 34, 377 (1901).

An attempt was made to determine the effect of the added oxidized state as would be expected from the reactions studied by Evans[1]. For this reason the observations were made in the .0263 normal sodium hydroxide to determine the effect due to the addition of acetate and of oxalate. The average minimum values were,

.054 molar acetaldehyde		−.153
.054 " "	+ sodium acetate, .020 N	−.158
.076 molar acetaldehyde		−.163
.076 " "	+ potassium oxalate, .020 N	−.160

The variations in the presence and absence of the added salt with time were the same.

Since it was not possible to secure reproducible results in acid solutions of acetaldehyde, chloral hydrate was studied. The decomposition of chloral hydrate in water was observed by titrating the acid formed by 100 ml. of the following solutions:

Chloral	Ml. .014 base			Maximum
hydrate	1/3 hr.	2 hr.	20 hr.	H^+
.0140 molar	1.4	1.4	2.2	.0003 N
.0280	2.6	2.7	2.8	.0004
.0560	2.7	3.9	4.2	.0006

The titration of hundredth normal acid after it had stood several days in the presence of chloral hydrate indicated that none of the chloral hydrate had decomposed.

The values given below are representative of the observations made during the first few minutes. Since the velocity of change is very great, the time is indicated in seconds to the nearest multiple of 5. To show the effect of changing acidity, results for .005 molar chloral hydrate only are given, except one series of observations to show the effect in acid solutions of the oxidized state, trichlor acetate.

.0050 molar chloral hydrate, .180 normal sulfuric acid

45 sec.	+.206	50 sec.	+.209	50 sec.	+.210
105	+.229	80	+.228	80	+.223
135	+.227	180	+.229	110	+.228
220	+.224	270	+.228	215	+.229

.005 molar chloral hydrate, .0180 normal sulfuric acid

35 sec.	+.181	35 sec.	+.179	75 sec.	+.188
90	.192	90	.192	120	.196
140	.198	130	.194	175	.199
290	.203	250	.199	220	.204
330	.204	495	.206		

---

[1] Evans: J. Am. Chem. Soc., **44**, 1543, 1730 (1922).

Same as preceding + .0046 molar sodium trichlor acetate

45 sec.	+.179	35 sec.	+.180	30 sec.	+.181
90	.190	85	.189	105	.196
165	.198	165	.196	160	.197
260	.202	265	.200	215	.198

.0050 molar chloral hydrate, .0062 N barium hydroxide

55 sec.	+.118	40 sec.	−.125	40 sec.	−.123
110	.120	90	.127	85	.128
160	.124	120	.125	215	.129
230	.123	275	.119	330	.125
280	.118	420	.116	650	.106
		900	.102	840	.103

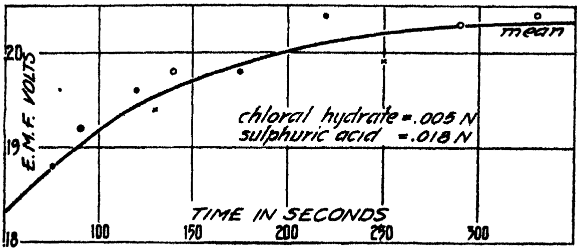


Fig. 2

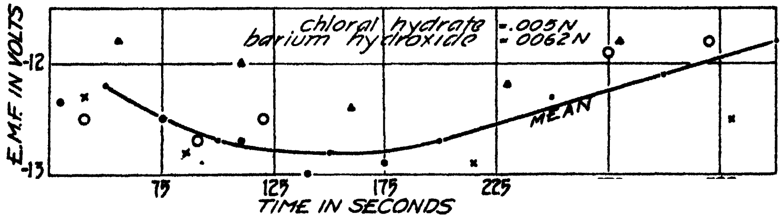


Fig. 3

Median curves to fit the data for the alkaline chloral hydrate solution, and the .018 normal acid solution are given in Figs. 2 and 3.

The velocity of decomposition of alkaline solutions of chloral hydrate was observed. The solutions were allowed to stand in the thermostat for the desired length of time, then the decomposition was stopped by adding an excess of standardized acid, and the excess acid was titrated with barium hydroxide solution, using phenol-phthalein as indicator. Since the reaction at this temperature was very rapid, especially for those in which the concentration of the base was relatively large, the results are not exceedingly accurate. The constants for reactions of the second order were calculated from the standard equations,

$$K_1 = \frac{1}{ta} \cdot \frac{x}{a - x}$$

and,

$$K_2 = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

A third constant, K_x, was calculated on the assumption, for calculation only, that the concentration of the reactive aldehyde was equal to the concentration of the base.

a = concentration of chloral hydrate,
b = concentration of barium hydroxide,
x = decrease in concentration of the base.

For b = a

t	b	x	K_1	t	b	x	K_1
0	.0070	.0000		0	.0560	.0000	
90 sec.		.00106	.283	60		.0263	.264
150		.00168	.301	120		.0363	.274
200		.00206	.298	200		.0425	.280
660		.00406	.299	325		.0471	.290
1140		.00493	.290				

For b = 2a

t	b	x	K_2	K_x
0	.00625	0		
15		00050	1.94	.42
60		.00139	1.80	.61
180		.00241	1.77	.57
250		.00276	2.02	.51
0	.01135	0		
40		.00304	2.00	.80
50		.00339	1.94	.78
75		.00420	2.07	.69

For a = 2b

t	b	x	K_2	K_x
0	.00595	0		
40		.00037	.137	.27
60		.00039	.097	.21
110		.00056	.077	.16
250		.00103	.068	.14

For acetaldehyde in alkaline solution the following facts only were observed: The base on standing in presence of the aldehyde did not change its concentration. For .054 and .144 acetaldehyde in .0263 normal sodium hydroxide, for the same intervals of time the same fraction of the aldehyde had decomposed when determined by the method given above.

Discussion of the Results

The oxidized state has no effect on the apparent electromotive force, a contrast to the reversible type of electrode.

The reduced state affects the apparent electromotive force proportionally to its concentration and to the concentration of the hydroyl ion, the same as for a reversible electrode like $H_2S - S^\circ$. The difference in the two curves in Fig. 2 is due to the fact that the reactive form may be formed less rapidly than in the ionization of the hydrogen sulfide. The subsequent rise in the curve in alkaline solution is due to the decomposition of this reactive form. The rise in the curve for acid solutions of chloral hydrate to a maximum is due to the decrease in concentration of this reactive form to a minimum by the formation of the inactive form.

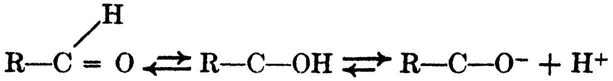
The velocity of decomposition of the chloral hydrate at first appears anomolous, but as shown by the approximation K_x, if we assume that the reaction is due to the active form whose equilibrium with the inactive form is determined by the concentration of the base, it may be possible to account for the variations of the constants for a dimolecular reaction.

The velocity of condensation of the acetaldehyde in a solution of a base of definite concentration is apparently a reaction of the first order.

The velocity of reduction, as reported by St. Bugarszky, for aldehydes is inversely proportional to the concentration of the hydrogen ion.

In all the preceding reactions of the reduced state and in the change of electromotive force, the concentration of the hydroxyl ion seems to be one of the determining factors.

By the assumption of the equilibrium reaction



$$R{-}\overset{\diagup H}{C}{=}O \rightleftarrows R{-}C{-}OH \rightleftarrows R{-}C{-}O^- + H^+$$

in which the bivalent carbon is the reactive form, all the preceding admit of simple interpretation,—the key is the fact that the bivalent carbon radical in solution is directly proportional to the concentration of the hydroxyl ion.

Then the apparent electromotive force, E_a, would be at 25°C, assuming the effect to be due to the bivalent carbon,

$$E_a = E_o - .06/n \log [RCHO] \quad [OH]$$

The changes of E_a as indicated by the curves for acid and alkaline solutions are due to the velocity of the change to equilibrium. This is reached in acid solutions of chloral hydrate in a few minutes, but in alkaline solutions the chloral hydrate, and the acetaldehyde decrease in concentration due to chemical reaction, and the curves reach a minimum value which would not be the true equilibrium values for the solutions as prepared.

In alkaline solutions, for the determinations made with one concentration of base, the velocity of condensation of the acetaldehyde is proportional to the concentration of the acetaldehyde. This indicates that the determining factor in the velocity of the reaction may be the formation of the bivalent carbon, and the latter condenses comparatively rapidly.

In neutral solution the chloral hydrate decomposes until a certain degree of acidity is reached. This is due to the decrease in concentration of the bivalent carbon form in the equilibrium reaction as stated above on account of the formation of the formic acid. In molar solutions of a base the velocity of decomposition of chloral hydrate is almost instantaneous, but in the concentrations of base where fairly accurate observations could be made, the concentration of the base seems to be the determining factor. From the above equilibrium reactions this may be interpreted as due to the dissociation of the ionized bivalent carbon form and its reaction with the base or with the water of the solution as an instaneous reaction, thus

$$Cl_3C\,.\,CO^- \qquad Cl_3C^- \;+\; {}^+CO^-$$

or

$$Cl_3C\,.\,CO^- + HOH \qquad Cl_3CH \;+\; HCOO^-$$

Summary

The apparent electromotive force of acetaldehyde and chloral hydrate was determined as affected by the concentration of the hydroxyl ion.

The velocity of decomposition of chloral hydrate in dilute alkaline solutions was studied.

A theory was advanced to correlate the observations,—the apparent electromotive force is due to the bivalent carbon radical in solution as the reduced state, which for this state has all the properties of the reduced state in an electrode that satisfies the conditions of a reversible electrode, but the oxidized state is passive.

University of Nebraska,
Lincoln, Nebraska.

STUDIES IN ADSORPTION. XIII.
SCHULZE-HARDY LAW AND ADSORPTION

BY N. R. DHAR AND S. GHOSH

In a previous report[1] of this series we made the following observations:—"It is of interest to note that those substances, which can form complex salts with the adsorbent are likely to be adsorbed most. Thus Ishizaka[2] has shown that potassium salicylate, potassium ferrocyanide and potassium oxalate are adsorbed most by $Al(OH)_3$. Similar results are obtainable with $Fe(OH)_3$. Evidently the phenomenon of adsorption is most marked when there is some sort of chemical affinity between the adsorbent and the substance, which is being adsorbed".

"It appears that hydrated manganese dioxide, which behaves like H_2MnO_3 and is also acid to litmus can adsorb large quantities of OH ions, because an acidic substance has naturally a great affinity for OH ions".

"We have observed that the basic portion adsorbed by hydrated manganese dioxide from substances like $BaCl_2$, $CuSO_4$, $Al_2(SO_4)_3$, $AgNO_3$, etc., cannot be removed by washing, whilst the basic portion adsorbed by hydrated manganese dioxide from NaCl, KCl, etc., can be removed slowly but completely by washing. Consequently the adsorption of the basic portion of these electrolytes is more or less permanent. Exactly similar results are obtained with hydrated silica, the basic portion adsorbed from NaCl, KCl, etc., can be removed slowly but completely by washing, whilst the basic portion adsorbed from $CuSO_4$, Alum, etc., cannot be removed by washing. Just as manganese dioxide is capable of adsorbing both acids and bases, similarly silica can adsorb both acids and bases and a base is more adsorbed than an acid, because silica is acidic in nature. The amount of adsorption of acids by silica is very small and is only a few percent of the total quantity of the acid taken. This adsorption is more or less due to the surface effect, and is allied to the adsorption of substances by charcoal, but the adsorption of bases by silica is connected with chemical affinity and is more permanent".

"Moreover it has been observed that the bigger the particles in a medium, the greater is its adsorption by an adsorbent".

"From our experiments on adsorption we find that substances like freshly precipitated $Fe(OH)_3$, hydrated MnO_2, etc., have marked adsorptive power and are in certain respects comparable to charcoal, whilst substances like As_2S_3, Sb_2S_3, $BaSO_4$, etc., have very slight adsorptive power, though all these substances can adsorb appreciably electrolytes in the course of their formation. Consequently the uncharged substances like As_2S_3, Sb_2S_3, etc., cannot adsorb the precipitating ions to any appreciable amount. Hence the amount of different ions adsorbed by As_2S_3, Sb_2S_3, etc., in the process of coagulation is more or less equivalent, as was shown by Whitney and Ober[1] and Freundlich[2]. On the other hand, the neutralized substances like hydrated MnO_2, $Fe(OH)_3$, etc., are capable of adsorbing appreciably the precipitating ions; hence in these cases the amount of ions adsorbed by a coagulating sol is bound to be different and are not in equivalent proportion".

---

[1] J. Phys. Chem., **28**, 457 (1924).

[2] Z. physik. Chem., **83**, 97 (1913).

"We are of the opinion that charge reversal, amount of adsorption and complex formation go hand in hand and depend upon the chemical affinity existing between the adsorbent and the substance which is being adsorbed".

In the same paper it was also observed that "In Weiser and Sherrick's[3] experiments on the adsorption of substances by $BaSO_4$ in the course of precipitation it is found that those ions which form sparingly soluble barium salts are adsorbed most, because sparingly soluble salts are more allied to barium sulphate". More or less similar results were obtained by us[4] in the adsorption of electrolytes by $BaSO_4$, obtained by the interaction of $Ba(OH)_2$ and H_2SO_4. Very recently Beekley and Taylor[5] have got similar results with AgI as the adsorbent. They have shown that less soluble salts are more strongly adsorbed and more soluble salts are weakly adsorbed by AgI.

In the same paper from a survey of the experimental results on adsorption and coagulation we have given a new interpretation of the Schulze-Hardy law when applied to adsorption experiments. Recently our interpretation of the Schulze-Hardy law has been adversely criticized by Weiser[6]. Our interpretation of the Schulze-Hardy law is that in general an ion, which has a small coagulating power for a colloid, is most adsorbed by the colloid in question. Inversely the greater the coagulating power of an ion the less is its adsorption. Hence it follows that an ion of higher valency is less adsorbed than an ion of lower valency. We shall prove in the following pages that this view of the Schulze-Hardy law is both theoretically and experimentally sound.

We shall first show that the interpretation of the Schulze-Hardy law hitherto held that the greater the valency of an ion the greater is its amount of adsorption is fallacious from the following arguments:—

(a) From experiments on coagulation of many sols with different electrolytes it is now established at least qualitatively that the greater the valency of the oppositely charged ion the greater is its coagulating power. This is really what is known as the Schulze-Hardy law, and this deduction is quite sound as it is based on experiments.

(b) Several workers in this field notably Freundlich[7], Bancroft[8], Weiser[9] and others have tacitly assumed that the greater the adsorbability of an ion the greater would be its coagulating power.

---

[1] J. Am. Chem. Soc., **23**, 842 (1901).
[2] Kolloid-Z., **1**, 321 (1907).
[3] J. Phys. Chem., **23**, 205 (1919).
[4] Kolloid-Z., **35**, 144 (1924).
[5] J. Phys. Chem., **29**, 942 (1925).
[6] J. Phys. Chem., **29**, 955 (1925).
[7] loc. cit.
[8] J. Phys. Chem., **19**, 349 (1915).
[9] loc. cit.

We shall show that this assumption has very little experimental support even in the adsorption of ions of the same valency not to speak of ions of different valencies.

Combining this assumption (b) which is not yet experimentally proved, with the deduction (a) which is experimentally sound, Freundlich and other workers in colloid chemistry have come to the conclusion that an ion of higher valency, which has a high coagulating power, is more adsorbed than an ion of low valency, which has small coagulating power.

We are of the opinion that this deduction is both experimentally and theoretically unsatisfactory. We believe that the Schulze-Hardy law that the greater the valency of an ion the greater is its coagulating power is generally applicable for the following reasons:—

Since the coagulation of an equal amount of a colloid by ions of different valencies, is at first an electrical phenomenon, it will be clear that for the charge neutralisation of a fixed amount of any colloid, the absolute amount of ions, expressed in gram-moles, necessary in the case of monovalent ions will be greater than that of bi- or trivalent ions, simply because the net charge on a bi- or trivalent ion is greater than that on a monovalent ion. It is apparent, therefore, that only for neutralization of charge on a sol, the greater the coagulating power of an ion the less would be its amount of adsorption.

Hence we are of the opinion that in the coagulation of a sol the valency factor of an ion is more important than its adsorbability. Previous workers in this field have given an undue importance to the question of adsorbability, which is no doubt of a great importance but is certainly not as great as that of valency. In this connection the following lines from an article by Freundlich[1] would be of interest:—

"It follows necessarily that the coagulative power of a given salt depends greatly both on the valency and on the adsorption coefficient, because with different (ionic) values, either of valency or adsorption, very different concentrations are necessary in the solution in order that the equivalent quantity of the (active) ion shall be adsorbed".

In order to prove our case we have to give a summary of the results obtained in adsorption experiments hitherto carried on.

Arsenious Sulphide

From the researches of Linder and Picton[2], Whitney and Ober, Freundlich[3], and Weiser on the coagulation of arsenious sulphide sol by different electrolytes, we find that the actual amount of adsorption expressed in millimoles is greater in the case of univalent ions like K, neufuchsin and aniline than in the case of bivalent ions like Ba, Sr, Ca, UO_2 or the trivalent ion Ce, which shows the least adsorption. It will be interesting to observe that the adsorption of ions per gram of As_2S_3 is small and varies from 0.021 to 0.082

---

[1] Burton: "Physical Properties of Colloidal Solutions", 182 (1921).

[2] J. Chem. Soc., 67, 63 (1895).

[3] Z. physik. Chem., 73, 385 (1910).

millimoles. This is certainly because as we have already emphasised that As_2S_3 is not a good adsorbent and the uncharged substance cannot adsorb the precipitating ions to a marked extent as will be shown from the direct experiments of Freundlich on the adsorption of electrolytes by a powder of As_2S_3. Hence the amount of different ions adsorbed by As_2S_3 in the process of coagulation is more or less equivalent as has been proved by different workers.

In this connection, it will be interesting to note that Weiser has made the following observations in one of his papers[1] on the adsorption of electrolytes by arsenious sulphide sol.

"The observations recorded in Table XI show conclusively that concentration of Li below the precipitation value have a marked effect on the adsorption of $Ba^{\cdot\cdot}$. Thus at the precipitating concentration of a mixture, containing 1/8 value of precipitating concentration of LiCl alone, the adsorption of Ba ion is lowered more than 25 per cent; whilst from a mixture containing one half the precipitation value of LiCl alone the adsorption of Ba is decreased 53 per cent. . . . The high precipitation value of LiCl cannot be due to a very low adsorption of Li ion, which would displace but little Ba ion at concentrations below the precipitation value; but is due to a fairly marked adsorption of Li ion associated with appreciable adsorption of the stabilizing chlorine ion within the concentration limits investigated".

Several years ago Freundlich[2] carried on some experiments on the adsorption of different electrolytes by powdered As_2S_3 and he found that the adsorption of ions in millimoles per gram of As_2S_3 from such electrolytes as NH_4Cl, $(NH_4)_2SO_4$, $Ce(NO_3)_3$, $UO_2(NO_3)_2$, para-chloraniline hydrochloride, etc. is very small and varies from 0.013 in the case of NH_4Cl to 0.023 in the case of para-chloraniline chloride for almost equal concentrations of the above electrolytes; whilst with morphine chloride, strychnine nitrate, neufuchsin, etc., the adsorption is much greater and varies from 0.068 to 0.050. Hence it is evident from the above results that the chemical affinity of As_2S_3 is more pronounced in the case of morphine hydrochloride, strychnine nitrate, neufuchsin, etc., than in the cations of other electrolytes.

It must be emphasised now that the adsorption of different ions by powdered As_2S_3 is essentially due to its chemical affinity for the ions in question. As these experiments were conducted with powdered As_2S_3, the question of charge neutralisation by the adsorption of ions cannot enter in these cases This important point seems to have been missed by several workers in this field because they have attempted to correlate the coagulating power of an ion and its adsorption from experiments carried on with the powdered substance and not the sol, and this is entirely unsatisfactory.

On comparing the results on adsorption obtained with the sol and with the powder of As_2S_3, we find that in general the adsorption of the same ion is greater with the sol than with the powder. The difference is mainly due to the amount of the ion necessary to neutralize the charge on the sol. From the foregoing results on the coagulation and adsorption by As_2S_3 sol as well as by powdered As_2S_3 we find that in general an ion of a higher valency is less adsorbed than an ion of a lower valency when the amount of adsorption is expressed in millimoles. In other words, when the adsorption is expressed in milliequivalents, the amount of adsorption is practically equal as has been first observed by Whitney and Ober. There is nothing in the experiments with As_2S_3 sol to show that the greater the valency of an ion the greater is the amount of its adsorption.

---

[1] J. Phys. Chem., **28**, 232 (1924).

[2] Z. physik. Chem., **73**, 385 (1910).

Antimony Sulphide

In a previous paper[1] we have shown that the adsorption of Ba ion by Sb_2S_3 sol is decreased to the extent of 55 percent by the presence of K ions below the precipitating concentration of KCl. We have also observed that the adsorption of K ion by Sb_2S_3 is also decreased by the presence of Ba ion. We have also proved that the adsorption of K (0.2571 millimole) ion expressed in millimoles is about 8 times that of Ba ion (0.0334 millimole) under identical conditions.

A very interesting fact has also been noticed that the sum of the adsorptions by Sb_2S_3 of K and Ba ions expressed in equivalents is greater than the adsorption of Ba ions by Sb_2S_3, when coagulated by $BaCl_2$ alone, but less than the adsorption of K ion when coagulated by only KCl. These results conclusively prove that univalent ions are more adsorbed than bivalent ones and are in support of our view that less the coagulating power of an ion the greater the adsorption.

Mercuric Sulphide

Freundlich and Schucht[2] have obtained the results given in Table I with a sol of mercuric sulphide.

TABLE I

Cation	Concentration of the sol grams per litre.	Coagulating power.*	Adsorption in millimole per gram of HgS.
NH_4	13.74	0.098	>0.05
Ag	11.74	3.57	0.02
Neufuchsin	13.74	10.31	0.008
Brilliant Green	8.38	20.83	0.004
Auramin	10.05	10.64	0.011
Methylene blue	14.96	10.31	0.0077
Ba	8.29	1.96	0.022
$Cu(Cu(NO_3)_2)$	8.26	6.67	0.015
$Cu(CuSO_4)$	14.43	3.85	0.011
Ce	10.45	12.19	0.004

* Coagulating power is the inverse of precipitation value in millimoles.

---

[1] Ghosh and Dhar: J. Phys. Chem., **29**, 435 (1925).

[2] Z. physik. Chem., **85**, 641 (1913).

Hence the order of the coagulating powers for the different electrolytes is Brilliant green > Ce > auramine > neufuchsin, methylene blue > Cu ($Cu(NO_3)_2$) > Cu ($CuSO_4$) > Ag > Ba > NH_4, beginning with the electrolyte of the highest coagulating power; whilst the order of the adsorption value is NH_4 > Ba > Ag > Cu ($Cu(NO_3)_2$) > Cu($CuSO_4$), auramine > neufuchsin > methylene blue > Ce > Brilliant green, beginning with the ion adsorbed most. From these results it is clear that the trivalent Ce ion, which has a very high coagulating power, is least adsorbed, whilst the monovalent ions like Ag, NH_4, etc., with low coagulating powers show greater adsorption. Hence these results of Freundlich and Schucht are in direct opposition to the views hitherto held that the greater the valency the greater the amount of adsorption, but are in support of our generalization that the greater the amount of adsorption the lower the valency. Though the results obtained by Freundlich and Schucht are not exactly comparable because they used sols of slightly different concentrations with different electrolytes, yet the general accuracy of our conclusion is beyond doubt as shown by these results.

In the foregoing pages it was emphasised that several workers have tacitly assumed that the greater the adsorbability of an ion the greater would be its coagulating power. The experimental results on HgS do not support this assumption even in the case of ions of the same valency not to speak of ions of varying valencies. Thus amongst the two simple univalent cations Ag and NH_4 the coagulating power of Ag ion is about thirty-five times greater than that of NH_4 ion, but the amount of adsorption is more than double with NH_4 than with Ag. Now, when we compare the coagulating powers of the four cations from the organic dyes the following order is obtained:—Brilliant green > auramine > methylene blue > neufuchsin. Their adsorptions are in the following order auramine > neufuchsin > methylene blue > Brilliant green. In the case of the divalent ions Ba and Cu, the coagulating power of Ba is less and the adsorption is greater than those of Cu obtained from either $Cu(NO_3)_2$ or $CuSO_4$. Hence it is clear that the assumption that the greater the adsorbability of an ion the greater is its coagulating power is not at all in accord with experimental results.

In this connection, it will be interesting to observe that the adsorption of the cations by a sol of HgS from the organic dyes is much less than that of other univalent cations. Their coagulating powers are much higher than those of other univalent ions; in other words, the univalent cations from dyes behave as polyvalent ions not only for the coagulation of HgS sol but also for a As_2S_3 sol as has been shown by Freundlich. We are of the opinion that the explanation of this particular behavior is the following:—

It is well known that many of these dyes are of a colloidal nature though they conduct electricity. We also know that the charge on a colloid particle is much greater than that on an ion. Moreover, we know from the Schulze-Hardy law that a polyvalent ion carrying several unit charges is a far better coagulant than an univalent ion; consequently the ionic micelles given out by an organic dye would behave as polyvalent ions, with a high coagulating power.

In a previous paper we have shown that the amount of adsorption by $BaSO_4$ is greater, the greater the size of the particles of the substance which is going to be adsorbed. Consequently the cations of the colloidal dyes are likely to be adsorbed in greater quantities than other simple univalent cations.

Freundlich determined the coagulating powers of several cations from dye stuffs on a sol of arsenious sulphide. He also determined the adsorption of these cations by powdered As_2S_3 as has already been reported. He observed that from dilute solutions of alkaloids or dyestuffs a great deal of adsorption of the organic cations takes place even with powdered As_2S_3 in comparison with the adsorptions of the other univalent ions like NH_4, Ag, etc. Moreover, it has been repeatedly observed that charge reversal can be readily effected by cations from alkaloids and dye stuffs. These results strongly support our view that amount of adsorption and charge reversal are essentially dependent on the chemical affinity of the adsorbent for the different cations.

The order of the coagulating power of different cations towards a sol of As_2S_3 is Ce > Al > neufuchsin > crystal violet > quinine sulphate > morphine chloride > UO_2 > Ba > Mg > p-chloraniline chloride > aniline chloride > strychnine nitrate > H > K > Na > Li—beginning with the ion of the highest coagulating power. It will be seen that though Ce, Al, etc., are less adsorbed by powdered As_2S_3 than any of the organic cations, the coagulating powers of trivalent ions Ce and Al are greater than those of the organic cations. Moreover, the coagulating powers of the bivalent ions like Ba, Mg, UO_2, etc., are greater than many organic cations like strychnine nitrate, aniline chloride, etc. Hence the contention that the greater the adsorbability the greater the coagulating power is not applicable to these cases.

It should be clearly pointed out here that no strict comparison between the coagulating power of an ion and its adsorption could be made from the experiments of Freundlich on As_2S_3, because in the majority of the adsorption experiments he has used a powder and not a sol of As_2S_3.

Ferric Hydroxide

The adsorption and coagulating powers of different acids by a sol of $Fe(OH)_3$, have been determined by Weiser and Middleton[1]. Their results are given in Table II.

TABLE II

Anion	Coagulating power	Adsorption in millimoles per gram of Fe_2O_3.
Phosphate	3.42	0.5721
Citrate	5.99	0.5081
Tartrate	4.21	0.6232
Oxalate	3.81	0.4364
Sulphate	4.12	0.3804
Iodate	1.67	0.7512
Dichromate	10.00	0.1559

---

[1] J. Phys. Chem., **24**, 30 (1920).

The above authors have concluded "It is evident that there is a tendency for the ions with the lowest precipitation values to be adsorbed the least and vice versa". Consequently it is clear from the experimental results of Weiser and Middleton that our conclusion that the greater the coagulating power the less the adsorption is experimentally sound.

Sen, in a thesis, has made a systematic study of the adsorption of different acids by freshly precipitated hydroxides of iron, aluminium, and chromium and he obtained the results given in Table III with freshly precipitated $Fe(OH)_3$.

TABLE III

Acid	Adsorption per gram adsorbent
Citric	0.8603
Oxalic	1.0325
Tartaric	0.9585
Sulphuric	0.8448

When the above acids are shaken with precipitated $Fe(OH)_3$ sols of positively or negatively charged $Fe(OH)_3$ are obtainable. Therefore, in all the adsorption experiments Sen has used a normal solution of KCl or NH_4Cl to coagulate the sols thus formed and in all cases the change in hydrogen ion concentration has only been estimated. Hence these results with precipitated ferric hydroxide are not comparable with those of Weiser and Middleton obtained with a sol of ferric hydroxide. But one fact comes out very prominently from these results that $Fe(OH)_3$ is a better adsorbent of acids and salts than As_2S_3. Moreover, the large amount of adsorption of the acids is mainly due to the chemical affinity of ferric hydroxide for these acids. Though a large amount of adsorption of acids is observed with precipitated $Fe(OH)_3$ it is useless to correlate this adsorption with the coagulating power of the electrolyte, because we are convinced that this high adsorption has nothing to do with the question of charge neutralization of the sol, but is essentially due to the chemical affinity of $Fe(OH)_3$ for the above acids.

Aluminium Hydroxide

In the adsorption of electrolytes by a sol of $Al(OH)_3$ or by precipitated $Al(OH)_3$, there is divergence amongst the results of different investigators. The following results are obtained by Gann[1] for a sol of $Al(OH)_3$, Table IV.

TABLE IV

Anion	Coagulating power	Adsorption in millimoles per gram Al_2O_3
Salicylate	0.125	0.30
Picrate	0.25	0.18
Oxalate	2.77	0.18
Ferricyanide	10.00	0.09
Ferrocyanide	12.50	0.073

---

[1] Kolloidchem.-Beihefte, **8**, 63 (1916).

It follows, therefore, from these results that the greater the coagulating power the less is the amount of adsorption and the greater the valency the less is the amount of adsorption.

On the other hand, the results obtained by Weiser and Middleton[1] are different from those of Gann. They are given in Table V.

TABLE V

Anion	Coagulating power	Adsorption in millimoles per gram Al_2O_3
Ferrocynaide	10.64	0.3202
Thiosulphate	5.32	0.4096
Ferricyanide	7.52	0.4046
Sulphate	3.75	0.4184
Oxalate	2.86	0.5710
Chromate	1.54	0.4352
Dithionate	1.23	0.3284
Dichromate	1.13	0.3185
Phosphate	2.89	0.8088

From the above results also it is evident that in the majority of cases the greater the coagulating power the less is the adsorption. It will be evident from the above results that $Al(OH)_3$ sol is a very good adsorbent for different ions, although Ishizaka has shown that 'grown alumina' can absorb ions to the extent only of 0.002 to .05 millimole per gram of the adsorbent. On the other hand Sen, has obtained the following results in the adsorption of acids by freshly precipitated $Al(OH)_3$:—

Acid	Adsorption in millimoles
Citric	0.783
Oxalic	0.952
Tartaric	0.933
Sulphuric	0.896

In this case also the amount of adsorption due to chemical affinity is more pronounced than that due to charge neutralisation, because the precipitated $Al(OH)_3$ can adsorb large quantities of acids.

From the above it will be seen that the results obtained by various investigators with a sol of $Al(OH)_3$ and different electrolytes are not concordant. In order to throw further light on the question of adsorption of different ions by $Al(OH)_3$ experiments on adsorption of substances by a $Al(OH)_3$ sol are in progress in this laboratory.

Chromium Hydroxide

No experiments are available on the adsorption of different electrolytes by a sol of $Cr(OH)_3$. Sen has, however, determined the adsorption of different acids by precipitated $Cr(OH)_3$, and he obtained the following results:—

---

[1] J. Phys. Chem., **24**, 630 (1920).

Acid	Amount adsorbed in millimoles
Citric	2.196
Tartaric	3.170
Sulphuric	3.919
Oxalic	4.106

These results show that acids are very highly adsorbed by $Cr(OH)_3$ and its adsorptive power is greater than that of either $Fe(OH)_3$ or $Al(OH)_3$.

In one of his recent papers Weiser has shown that as the concentration of $K_2C_2O_4$ is increased above the precipitation value the amount of adsorption of C_2O_4 ion also increases. This only proves that freshly precipitated $Cr(OH)_3$ has a great affinity for oxalate ions.

Consequently from the experimental results of Sen and of Weiser we conclude that the adsorption of the oxalate ion by freshly precipitated $Cr(OH)_3$ due to chemical affinity will be more prominent than that due only to charge neutralisation of a sol of $Cr(OH)_3$. Hence it is absolutely useless to conclude that oxalate ion, because of its higher valency is more adsorbed than chloride ion as has been done by Weiser, as nobody as yet determined the adsorption of chloride ions by a sol and by freshly precipitated $Cr(OH)_3$ in order to show whether the adsorption of chloride ions by precipitated $Cr(OH)_3$ due to chemical affinity is more pronounced than the adsorption necessary only for charge neutralization of the sol.

Manganese Dioxide

In previous papers[1] we found that the adsorption of ions by manganese dioxide in the course of its formation is in the following order:—

$Ag > Na > Li > Cu > Cd > Ba > Ni, Zn > UO_2 > Th > Al$. This shows that in general ions of lower valency are more adsorbed than ions of higher valency in the precipitation of manganese dioxide.

We also measured the adsorption of cations by precipitated manganese dioxide and the order of adsorption is the following:—

$$Ag > Cu > Cd > Zn, Mg > Ba > Sr, Ca > Al$$

Very recently we have again measured the adsorption of different cations by a sol of manganese dioxide as well as by precipitated manganese dioxide of a great purity.

The sol was prepared by the interaction of $KMnO_4$ and H_2O_2 and dialysed for a week and completely freed from alkali, and it contained 1.6 grams MnO_2 per litre. 20 c.c. of this sol were taken and 10 c.c. of M/10 solutions of different electrolytes were added and the volume was always made up to 50 c.c. The following results are obtained:—

---

[1] Ganguli and Dhar: J. Phys. Chem., **26**, 701, 836 (1922); Chatterji and Dhar: Kolloid-Z., **33**, 18 (1923).

Cations	Adsorption in millimole per gram of MnO_2
K	5.514
Ag	5.85
Cu($CuSO_4$)	3.90
Cu($CuCl_2$)	5.095
Ba	1.98
Al	0.03 (approx.)

The order of adsorption of cations by a pure sol of manganese dioxide is Ag > K > Cu > Ba > Al.

From the foregoing results obtained with a pure sol of MnO_2, we can conclude that the higher the valency of an ion the less is the amount of its adsorption. This result is in direct opposition to the view hitherto held that an ion of a higher valence would be more adsorbed than that of a low valence.

From our recent experiments with freshly precipitated, well-washed and an air-dried sample of hydrated manganese dioxide the following results are obtained:—

Cation	Amount adsorbed in millimole per gram of the adsorbent
K	1.159
Ag	1.518
Cu($CuSO_4$)	1.131
Cu($CuCl_2$)	1.048
Ba	0.386
Al	0.083

The order of adsorption of cations by pure hydrated manganese dioxide is Ag > K > Cu > Ba > Al. In this case also we find ions of higher valency are less adsorbed than ions of lower valency. These results as obtained now are in agreement with those already published.

In this connection we have to emphasise the fact that the adsorption of ions is much greater by a definite weight of the adsorbent in the course of its formation than that obtained when the same weight of the absorbent prepared long ago is used. We have repeatedly observed that sols of $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, MnO_2, etc., are much better adsorbent of ions than the precipitated substances. Moreover, the adsorbability of ions decreases with the ageing of the precipitates. When a sol is coagulated by an electrolyte, the neutralisation of the charge takes up a definite quantity of the oppositely charged ion, and if the neutral particles thus formed have a very slight chemical affinity for the coagulating ion we should always find that the adsorption for different ions expressed in equivalents should be practically equal just as we get in the case of As_2S_3 sol to a certain extent. When the adsorption is expressed in moles per gram of the adsorbent, as has been done in this paper we ought to find that the greater the valency of the ion the less is its adsorption.

We have systematically expressed the amount of adsorption of ions in millimoles, and not in milliequivalents as has been done by other workers.

It is easy to conceive that in the coagulation and adsorption by sols, ions take part as a whole and not in parts, and consequently the expression of the results of adsorption and coagulation in millimoles and not in milliequivalents seems more sound and the results of coagulation and adsorption when expressed in millimoles seem more readily conceivable.

We have already emphasised that many authors notably Freundlich, Weiser and others have assumed that the greater the adsorbability of an ion the greater will be its coagulating power. This assumption seems apparently reasonable specially with ions of the same valency, because along with the electrical attraction of the oppositely charged ion towards the sol particles, the chemical affinity between the sol and the coagulating ion may help in the coagulation of the sol because we know that the greater the chemical affinity of an ion towards an adsorbent the greater is its adsorbability. But unfortunately the experimental results available in this field do not support this assumption and it seems likely that there is some unknown factor, which counteracts the effect of chemical affinity of an ion for a sol in facilitating its charge neutralization and coagulation. The assumption that greater the adsorbability the greater the coagulating power will be disproved from the following experimental results even in the case of ions of the same valency:—

Sol	Anion	Adsorption in millimole per gram of the adsorbent	Coagulating power	Author
				Weiser and Middleton
$Fe(OH)_3$	SO_4	0.3804	4.12	”
”	C_2O_4	0.4364	3.81	”
$Al(OH)_3$	SO_4	0.4984	3.72	”
”	C_2O_4	0.5710	2.86	”
$Al(OH)_3$	Picrate	0.18	0.25	Gann
”	Salicylate	0.30	0.125	”

It is well known that a solution of $K_2C_2O_4$ is more hydrolysed and contains more OH′ ions than a solution of K_2SO_4 of the same concentration. Consequently in presence of $K_2C_2O_4$ the positively charged $Cr(OH)_3$ sol will be more unstable than in presence of the same concentration of K_2SO_4. Hence if we take into account the hydrolysis and the hydrogen ion concentration in solutions of $K_2C_2O_4$ and K_2SO_4 a solution of $K_2C_2O_4$ should coagulate a sol of $Cr(OH)_3$ in a smaller quantity than K_2SO_4. Hence the suggestion of Weiser based on hydrolysis to explain the difference in the behavior of $K_2C_2O_4$ and K_2SO_4 is of no avail.

Ishizaka has determined the coagulating power of various anions towards a sol of $Al(OH)_3$ and he has also determined the adsorption of the same anions by "grown alumina". He has observed that potassium salicylate is about nine times more effective coagulant than KCl, the coagulating power of salicylate ion is 187.7 whilst that of chloride ion is 21.9.

From the adsorption curves obtained by Ishizaka of various ions with 'grown alumina' we find that the adsorption of 0.02 millimole is reached at concentrations 0.046M in the case of chloride and 0.001M in the case of salicylate. Now, if the view that the greater the adsorbability of an ion the greater would be its coagulating power be correct, the coagulating power of the salicylate ion should be 46 times greater than that of the chloride ion, but in actual experiment we find that the ratio of the two coagulating powers is nine, instead of the calculated value 46.

In the case of substances like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, MnO_2 etc., the chemical affinity of these substances for the coagulating ions is much more pronounced than in the cases of As_2S_3, Sb_2S_3 etc. Consequently the correlation between the coagulating powers or the valencies of ions with their amount of adsorption in the cases of sols like $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, MnO_2, etc., is less satisfactory than in the cases of As_2S_3, HgS and Sb_2S_3 sols because the precipitates of the latter class of substances have a small chemical affinity for their coagulating ions.

If by any means we can find out the amounts of adsorption of an electrolyte by a definite weight of the sol and by its freshly obtained precipitate as soon as it is formed, we shall find that this difference of the two adsorption values expressed in moles would be greater in the case of univalent ions than polyvalent ions, because this difference arises from the adsorption due only to charge neutralisation of a sol and to this difference only the Schulze-Hardy law should be rigidly applicable.

Barium Sulphate

From our experiments on the adsorption of different anions by $BaSO_4$ obtained by the interaction of equivalent amount, of $Ba(OH)_2$ and H_2SO_4, we obtain the following order of adsorption:—$Cr_2O_7'' > S_2O_3'' > BrO_3' > AsO_3''' > C_2O_4'' > IO_4' > IO_3' > MnO_4' > NO_2' > Fe(CN)_6'''' > Fe(CN)_6''' > Cl' > CNS' > Br' > I'$ whilst Weiser and Sherrick working with different barium salts and K_2SO_4 obtained the following order:—

$$NO_3' > NO_2' > ClO_3' > Fe(CN)_6'''' > MnO_4' > Cl' > Fe(CN)_6''' > Br' > CN' > CNS' > I',$$

the results are expressed in millimoles. It will be observed from the above results that in general monovalent and bivalent anions are more adsorbed than tri- or tetravalent anions. The adsorption series as obtained by us or by Weiser and Sherrick are not in complete agreement with our interpretation of the Schulze-Hardy law, because the positively charged $BaSO_4$ is capable of adsorbing positive ions as well, and the neutral molecule of $BaSO_4$ can also adsorb the negative ion, the positive ion or the neutral molecule of the electrolyte.

Our experiments on the precipitation of $BaSO_4$ in the presence of KCl and $K_2C_2O_4$, show that the adsorption of C_2O_4'' ion is greater than that of Cl' ion, though according to our view of the Schulze-Hardy law it should be otherwise. We have found that along with the adsorption of C_2O_4'' ion by $BaSO_4$ appreciable quantities of K ions are also adsorbed. The positively charged $BaSO_4$ can adsorb K ions from $K_2C_2O_4$ and hence more of the oxalate ion would be necessary for the charge neutralisation and precipitation, whilst in the case of KCl no K ion is adsorbed. Hence a small amount of Cl ion is enough for charge neutralisation. From the following experimental results it will be seen that Na ions from Na_3AsO_3 and K ions from $K_2C_2O_4$ are adsorbed by $BaSO_4$:—

Electrolyte	Original concentration	Percentage of adsorption
Na_3AsO_3	0.08833 M	3.7
$K_2C_2O_4$	0.06894 M	2.0

It is evident, therefore, that a colloid can actually adsorb an ion carrying the same charge as the sol and this adsorption stabilises the sol. Consequently if the amount of this adsorption is large, deviations from Schulze-Hardy law will take place.

Freundlich has repeatedly emphasised that when there is no complication, the values of *a* and *n* in his exponential formula $x = ac^n$, should be the same for all electrolytes. In other words, according to Freundlich, the adsorption curve of ions with a certain sol should be the same irrespective of the valency of the coagulating ion. If we accept this view of Freundlich, which has been questioned by Wo. Ostwald[1], it follows that the amount of adsorption of a trivalent ion and an univalent ion should be equal at the same original concentration; consequently, it has not been proved at all that an ion of higher valency is adsorbed more than an ion of lower valency.

Curiously enough the majority of experiments on adsorption and coagulation carried on by different investigators are strongly in support of our view that the smaller the coagulating power of an ion the greater is its amount of adsorption. Thus the experiments of Freundlich and Schucht on the coagulation and adsorption by a sol of mercuric sulphide our experiments on Sb_2S_3, the coagulation and adsorption experiments of Gann on $Al(OH)_3$ sol and on $Fe(OH)_3$ sol by Weiser and Middleton, and our experiments on a sol of manganese dioxide conclusively prove that the greater the valency of an ion the less is its amount of adsorption and the smaller the coagulating power of an ion the greater is its amount of adsorption.

Another interesting fact which is observed from a survey of the experimental results is this:—

Our experiments on the adsorption of cations by precipitated hydrated MnO_2 conclusively prove that even with the precipitate, an ion of higher valency is adsorbed much less than an ion of lower valency.

When comparisons are made in the adsorption of ions like NH_4, Ba, UO_2, Ce, etc., by powdered As_2S_3 we also find that there is a general tendency of the ions of lower valency to be adsorbed more than ions of higher valency at equal concentrations of the electrolytes. It is evident that in these cases the question of charge is unimportant, because the adsorbents are neutral substances. It is very difficult to explain these facts in the present state of our knowledge on the mechanism of adsorption, but we are throwing out the following tentative suggestion:—

---

[1] Kolloid-Z., **26**, 28, 69 (1920).

If we consider that the chemical affinity of K and Ba ions for hydrated manganese dioxide to be practically equal and if we assume that two K ions are adsorbed by an unit surface of hydrated manganese dioxide, the force of repulsion between these two ions is e^2/r^2, where e is the charge on an univalent ion r, the distance between the ions. Hence the force of repulsion between two bivalent ions will be $4e^2/r^2$ on the assumption that two barium ions could be taken up by an unit surface of MnO_2. Since the force of repulsion for a bivalent ion is 4 times greater than that for a monovalent ion, it is reasonable to expect that less of Ba ions would be adsorbed than K ions on an unit surface of the hydrated manganese dioxide under otherwise identical conditions.

Many authors have deduced the adsorbability of different ions from their coagulating powers towards a certain sol. It is well known that in alkaline medium albumin is negatively charged and cations are effective in coagulating albumin, whilst in the presence of acids the albumin is positivelty charged and the anions are effective. Bancroft[1] has arranged cations and anions in series of gradually increasing or decreasing adsorptive power from the coagulating powers of the anions on a positively charged sol, and from those of the cations on a negatively charged sol.

In view of the facts brought forward in this paper these adsorption series obtained from the coagulating powers seem untrustworthy.

Summary

1. The generally accepted view that an ion, which is highly adsorbed also possesses a high coagulating power is not supported by experiments on adsorption.

2. There is no justification for the assumption that the greater the valency and hence the coagulating power of an ion the greater is its adsorption.

3. On the other hand, experiments on the coagulation and adsorption of different ions by sols of HgS, Sb_2S_3, $Al(OH)_3$, $Fe(OH)_3$, MnO_2 etc., strongly support our view that the greater the valency of an ion the less is its amount of adsorption and smaller the coagulating power of an ion the greater is its amount of adsorption.

4. It has been shown that the large amount of adsorption of ions associated with the coagulation of the sols like MnO_2, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ etc., is mainly due to a marked chemical affinity of these substances for different ions.

5. It seems very likely that the valency of an ion is a more important factor in coagulation than its adsorbability.

Chemical Laboratory,
University of Allahabad,
Allahabad, India
September 23, 1925.

---

[1] J. Phys. Chem., 19, 349 (1915).

VAPOR PRESSURE LOWERING AS A FUNCTION OF THE DEGREE OF SATURATION. II

BY ISAAC BENCOWITZ* AND HENRY T. HOTCHKISS, JR.

Introduction

Despite the fact that concentration is a variable of primary importance, no uniform mode of expressing the ratio of the quantity of one substance to another, or to their sum has ever been employed. For analytical purposes the choice of a system of units is more or less a matter of expediency, but in the study of the theory of solutions a method of expressing concentrations which is of theoretical significance is essential. Several ratios have been proposed and used in an attempt to fulfill this requirement, but none has been found to be on a sound basis. Thus the "volume-normal" system, i.e. number of moles per litre of solution, had theoretical significance because van't Hoff's discovery[1] of the analogy between the osmotic pressure of solutions and the behavior of gases. Later Morse and Fraser[2] in order to bring this very analogy in closer agreement with the experimental facts, introduced the "weight-normal" system, i.e. number of moles of solute in 1000 gms. of water. Since then, it has been definitely shown[3] that no parallelism between the gas and the osmotic pressure of solutions exists. The theoretical foundations on which these two systems had been based were thus shown not to be sound. The methods themselves, however, remain and are frequently used. Of the two, the "weight-normal" system is preferred by many investigators[4] on various grounds.

Duhem[5] expressed the concentration in moles of the dissolved substance per mole of solvent. In all these systems one of the components is designated as solute and the other as solvent. A more symmetrical manner of expressing the concentration is the "mole-fraction". This system assumes a theoretical significance because of Raoult's law. But this law supposedly valid in the case of infinitely dilute solutions cannot accurately define even the so-called "ideal" solutions[6]. Rodebush[7] states "that even in the most dilute solutions that we can study, the attraction between ions causes a negative deviation from Raoult's Law". The mole-fraction, however, has numerous theoretical and practical advantages[1]. Still another method which has been found useful in expressing solubility, is number of gram-moles of water required to dissolve one gram-mole of solute[2]. The mole-fraction, however, has numerous advantages in the theoretical application of thermodynamics to the theory of solutions[3].

---

* National Research Fellow in Chemistry.

[1] Z. physik. Chem., 1, 481 (1887).

[2] Am. Chem. J., 34, 1 (1905); 37, 324, 425, 458 (1906); 38, 175 (1907); Morse: "The Osmotic Pressure of Aqueous Solutions", p. 97 (1914); Findlay: "Osmotic Pressure" (1913); Bancroft: J. Phys. Chem., 10, 320 (1910).

[3] Lewis: J. Am. Chem. Soc., 30, 660 (1910); Kendall: 43, 1391 (1921); Hildebrand: "Solubility", p. 24 (1924).

[4] Lewis and Randall: "Thermodynamics", p. 33 (1923); Philip: J. Chem. Soc., 91, 711 (1907).

[5] Duhem: "Méranique chimique", 3, 4 (1898).

[6] Hildebrand: "Solubility", p. 27 (1924).

[7] J. Phys. Chem., 28, 1115 (1924).

All these various ways of expressing concentrations are arbitrary, from a theoretical point of view. The only criterion for the choice of the method to be employed seems to be its usefulness. Such a criterion is scientifically illogical and all functions in which the concentration expressed in any of these ways appears as a variable become arbitrary.

If it were possible to express the concentration in such a manner that it would become a function of the solution as much as any other property of the solution, then the method of expression would be of fundamental significance. Now if we designate the concentration thus expressed by S, and the solution forces by X, we can write,—

$$S = f(X) \tag{1}$$

and if we take any other property, A, of a solution we can write

$$A = \varphi(X) \tag{2}$$

so that if it were possible to express A as a function of S we would obtain,

$$A = F(S) \tag{3}$$

Relation (3) is bound to be a fundamental expression and it may tell us something concerning the forces of solution X. There is nothing arbitrary about this function, inasmuch as both variables are functions of X.

Vapor Pressure Lowering and Degree of Saturation

The degree of saturation is the concentration of a solution expressed in terms of the solubility. Thus if the concentration of a solution is given as n gms. (or moles) per W gms. (or moles) of solvent, and the concentration of a saturated solution as N gms. (or moles) per W gms. (or moles) of solvent, the degree of saturation S, is then given by:

$$S = n/N$$

The degree of saturation is therefore the concentration of a solution expressed in terms of solubility. The concentration thus expressed is fundamental, and obviously, is as much a function of the solution forces as the solubility. And all relations expressing any property of the solution as a function of the degree of saturation will be essentially fundamental.

Applying the concept of the degree of saturation to vapor pressure lowering, the following relation was developed[4].

$$\log \Delta P = K \left[\frac{1}{T} - a\left(1 - \frac{\log S}{b}\right) \right] \tag{4}$$

---

[1] Lewis and Randall: loc. cit.; Bjerrum: Z. physik. Chem., **104**, 406 (1923); John Johnston: J. Phys. Chem., **29**, 882 (1925).

[2] Gladstone and Pound: J. Chem. Soc., **127**, 2660 (1925).

[3] Lewis and Randall: loc. cit.; John Johnston: J. Phys. Chem. **29**, 882 (1925).

[4] Bencowitz: J. Phys. Chem., **29**, 1432 (1925).

The similarity between solubility and vapor pressure is best shown in the following quotation from Nernst[1]. "The far-reaching analogy which exists between the process of solution and that of evaporation, and to which repeated reference must be made, is also shown in the fact that just as the vapor pressure of a solvent is depressed by the addition of a foreign substance *B*, so also is the solubility of *A* in a second solvent diminished by the addition of a foreign substance *B*". In the case of *non-volatile solutes*, this statement is not valid inasmuch as we do know of instances where the addition of a foreign substance *B* increases the solubility[2] whereas no instances are known where the same is true of the vapor pressure. The solubility and vapor pressure are, therefore, hardly identical, but they are, no doubt, similar processes. Equation (4) is therefore identical with (3) since the two variables the vapor pressure lowering, $\triangle P$, and the degree of saturation, S, are both functions of the same solution forces. This relation is of a fundamental nature.

Equation (4) was obtained in the following manner on the basis of three postulates:

Postulate 1. When the log of the vapor pressure lowering $\triangle P$ for any degree of saturation S is plotted against the reciprocal of the absolute temperature T, a straight line should be obtained.

$$\left[\frac{\partial \log \triangle P}{\partial (1/T)}\right]_S = K$$

Postulate 2. The value of the constant K is independent of the degree of saturation.

Postulate 3. When the log of the degree of saturation S is plotted against the reciprocal of the absolute temperature at constant vapor pressure lowering ($\triangle P$ = 1 mm.) a straight line should be obtained, i.e.,

$$\left[\frac{\partial \log S}{\partial (1/T)}\right]_{\triangle P = 1\text{ mm}} = \text{Const.}$$

The experimental proof of these three postulates as well as the mathematical derivation is given in the first paper[3]. In the present paper additional experimental evidence will be given in corroboration of equation (4) and of Postulate 1.

Generalization 1.

According to the first postulate,

$$\left[\frac{\partial \log \triangle P}{\partial (1/T)}\right]_S = K$$

which upon integration gives for the limits $\triangle P'$ and $\triangle P''$,

$$\log \frac{\triangle P'}{\triangle P''} = K\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad . \tag{6}$$

---

[1] Nernst: "Theoretical Chemistry", 5th English Ed., p. 147 (1923).

[2] K. Linderstrom-Lang: Compt. rend. Trav. Lab. Carlsberg, 15, 1 (1924). See Eucken, Jette and LaMer: "Fundamentals of Physical Chemistry," 342 (1925).

[3] Bencowitz: loc. cit.

A similar expression where $S = 1$, i.e. for the vapor pressure lowering of a saturated solution at T_1 and $-T_2$ is,

$$\log \frac{\Delta P_S'}{\Delta P_S''} = K\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (7)$$

TABLE I

Ratios of Vapor-pressure Lowering at any Degree of Saturation to that of a Saturated Solution at the Same Temperature

Name of Substance	t	ΔP_s	ΔP_1	$\Delta P_1/\Delta P_s$	ΔP_2	$\Delta P_2/\Delta P_s$
$NaBr \cdot H_2O$	50	40.65	21.8	0.4456	9.75	0.1991
	60	80.54	36.1	.4488	16.1	.2004
	70	131.5	58.4	.4436	26.3	.2000
	80	200.0	88.0	.4405	39.4	.1972
	90	301.3	133.5	.4426	60.0	.1991
				*A.D. = 0.5%		A.D. = 0.1%
$K_2CO_3 \cdot 2H_2O$	30	18.11	7.60	.4198	3.20	.1766
	40	31.62	13.59	.4249	5.78	.1807
	50	53.95	23.07	.4246	9.93	.1828
	60	95.06	39.63	.4169	16.86	.1774
	70	149.6	63.53	.4246	26.91	.1799
	80	235.5	100.0	.4246	42.46	.1803
	90	367.2	153.8	0.4188	64.86	.1766
				A.D. = 0.7%		A.D. = 1.1%
K_2CrO_4	40	8.61	3.89	.4524	1.77	.2055
	50	14.90	6.79	.4560	3.11	.2090
	60	24.77	11.22	.4529	5.13	.2070
	70	38.91	17.74	.4560	8.18	.2104
	80	60.25	27.55	.4571	12.62	.2094
	90	92.05	41.30	.4488	18.45	.2005
				A.D. = 0.5%		A.D. = 1.3%
$BaCl_2 \cdot 2H_2O$	50	9.50	4.82	.5069	2.11	.2218
	60	16.22	8.36	.5152	3.73	.2286
	70	26.61	14.09	.5157	6.33	.2377
	80	44.67	22.91	.5140	10.23	.2291
	90	68.87	35.65	.5145	16.29	.2366
				A.D. = 0.5%		A.D. = 2.0%
$(NH_4)_2SO_4$	30	6.15	3.10	.5035	1.56	.2530
	40	11.20	5.66	.5058	2.86	.2559
	60	32.96	16.33	.4954	8.18	.2483
	70	52.24	26.18	.5012	13.24	.2535
	80	82.60	41.50	.5034	20.75	.2512
	90	124.7	62.23	.4943	31.12	.2511
				A.D. = 0.7%		A.D. = 0.7%

* A.D. = The average deviation from the average.

TABLE I (continued)

Name of Substance	t	ΔP_s	ΔP_1	$\Delta P_1/\Delta P_s$	ΔP_2	$\Delta P_2/\Delta P_s$
$MgCl_2 . 6H_2O$	40	37.16	14.19	0.3733	5.36	0.1386
	60	112.7	41.88	.3715	15.56	.1380
	80	290.4	107.9	.3715	39.63	.1365
				A.D. = 0,16%		A.D. = 1.2%
$SrCl_2 . 6H_2O$	30	9.77	3.96	.4074	1.62	.1663
	40	19.41	7.92	.4083	3.25	.1675
	50	35.97	14.62	.4065	5.96	.1656
	60	67.30	27.48	.4083	11.20	.1663
				A.D. = 0.6%		A.D. = 8%
$SrBr_2 . 6H_2O$	50	57.55	21.38	0.3715	8.57	0.1479
	60	105.9	39.35	.3715	14.86	.1403
	80	316.2	118.9	.3758	45.50	.1439
				A.D. = .5%		A.D. = 1.0%
LiCl	40	20.65	8.00	.3873	3.57	.1730
	50	35.89	14.45	.4027	6.21	.1730
	60	63.38	25.59	.4036	10.89	.1718
	65	79.08	32.21	.4074	14.06	.1758
	70	100.5	42.17	.4198	17.99	.1791
	75	129.4	53.96	.4169	22.91	.1770
				A.D. = 2.0%		A.D. = 1.3%
NH_4Cl	40	13.46	7.13	.5296		
	50	24.77	13.24	.5358		
	60	43.55	23.50	.5395		
	70	72.78	38.46	.5284		
	80	118.3	64.86	.5483		
				A.D. = .1%		
KI	40	17.30	8.12	.4699	3.76	.2172
	50	32.88	15.74	.4787	7.21	.2193
	60	58.75	27.60	.4699	12.88	.2193
	70	95.72	45.60	.4765	21.53	.2249
	80	159.2	75.17	.4721	34.99	.2193
	90	252.3	118.9	.4710	55.08	.2183
				A.D. = 0.6%		A.D. = 0.8%
RbCl	30	9.50	4.46	.4688	2.08	.2193
	40	17.22	8.09	.4699	3.80	.2208
	50	30.76	14.52	.4721	6.92	.2249
	60	53.57	25.07	.4678	11.70	.2183
	70	87.70	40.55	.4624	19.05	.2173
	80	136.8	64.27	.4699	30.13	.2203
	90	210.4	98.85	.4699	46.78	.2223
				A.D. = 0.7%		A.D. = 0.9%

TABLE I (continued)

Name of Substance	t	ΔP_s	ΔP_1	$\Delta P_1/\Delta P_s$	ΔP_2	$\Delta P_2/\Delta P_s$
KCl	20	2.58	1.38	.5370	1.43	.2723
	30	5.13	2.73	.5321	1.31	.2559
	40	9.75	5.03	.5165	2.44	.2500
	60	30.20	15.14	.5012	7.53	.2495
	70	49.20	25.18	.5117	12.36	.2512
	80	81.28	40.74	.5012	20.05	.2466
	90	123.3	62.95	.5105	31.26	.2535
				A.D. = .2%		A.D. = 2.0%
$BaBr_2 . 2H_2O$	40	15.96	6.73	0.4217	2.84	.1778
	60	46.66	19.63	.4207	8.32	.1782
	80	120.30	50.93	.4217	21.58	.1786
				D.A. = .1%		D.A. = .1%
$ZnSO_4{\cdot}H_2O$	70	30.34	15.21	.5012	7.62	.2512
	80	44.77	22.39	.5000	11.17	.2495
	90	64.27	32.14	.5000	16.11	.2506
				A.D. = 0.8%		A.D. = .2%
$NaBr . H_2O$	50	47.87	21.62	.4519	9.82	.2051
	60	79.80	35.81	.4488	16.00	.2005
	80	192.7	87.5	.4539	39.45	.2046
	90	292.4	131.8	.4508	59.28	.2028
				A.D. = .3%		A.D. = .8%
$NaI . 2H_2O$	30	22.13	9.59	.4335	4.17	.1883
	40	42.85	18.41	.4375	7.44	.1862
	50	81.65	35.72	.4325	15.21	.1866
	60	152.80	66.08	.4299	28.51	.1854
				A.D. = .5%		A.D. = .4%

Subtraction (7) from (6) and dropping logs, we get,

$$\frac{\Delta P'}{\Delta P_S'} = \frac{\Delta P''}{\Delta P_S''}$$

That is, the ratio of the vapor pressure lowering at any degree of saturation, and the vapor pressure lowering of a saturated solution is independent of the temperature. In Table I are given the theoretical and experimental values of these ratios. The experimental values were read off smooth log S − log ΔP curves which passed through the various experimental points. A family of such curves is shown in Fig. 1. The ΔP_1 and ΔP_2 values, given in the third and fifth columns of Table I, were read off these isotherms for Log S = 0.3

and log S = 0.6 respectively. The choice of log S was a matter of convenience. The vapor pressure lowering of a saturated solution, ΔP_s, at each temperature was obtained by extending the straight line log S − log ΔP to log S = O. These values are given in the second column of Table I. Comparison data of seventeen electrolytes are given. For the other substances the extrapolation must be carried too far to be reliable. It is seen, therefore, that Generalization 1 is substantially corroborated by the experimental data. In only a few cases is the average deviation greater than one per cent.

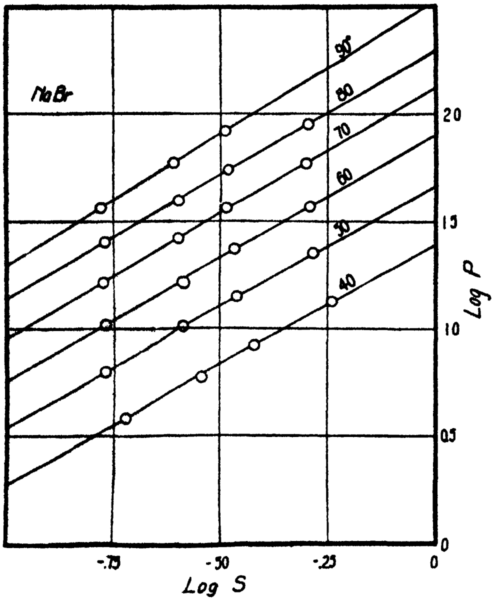


FIG. 1

Log P–log S curves for Sodium Bromide

Generalization 2

Equation (4) may be written,—

$$\log \Delta P = K\,[1/T - a] + Ka/b \log S \qquad (4)$$

For a saturated solution, since log S = O, we have

$$\log \Delta P_S = K\,[1/T - a] \qquad (8)$$

subtracting (8) from (4)

$$\log \Delta P/\Delta P_S = Ka/b \log S \qquad (9)$$

which on dropping logs and letting Ka/b = h, becomes

$$\Delta P/\Delta P_s = S^h \qquad (10)$$

TABLE II

Comparison Values of the Ratios $\Delta P/\Delta P_s$ and S

Name of Substance	t	ΔP	$S \times 10^2$	$\Delta P/\Delta P_s$	S^h	ΔP	$S \times 10^2$	$\Delta P/\Delta P_s$	S^h
NaI . $2H_2O$	30	3.90	23.69	0.1762	0.1743	9.10	47.37	0.4112	.4040
	40	6.79	21.96	.1574	.1590	99.60	29.29	.2225	.2254
	50	11.40	19.75	.1386	.1398	16.00	26.34	.1946	.1983
	60	18.40	17.53	.1202	.1209	42.90	35.04	.2802	.2810
$MgCl_2$. $2H_2O$	40	3.20	17.40	0.08224	0.08144	19.18	60.93	0.4930	0.4908
	60	8.40	16.39	.07452	.07473	22.70	32.76	.2014	.2019
	80	51.60	30.25	.1776	.1800	116.1	52.94	.3998	.4018
$SrCl_2$. $6H_2O$	30	24.0	34.07	0.2445	0.2482	41.0	51.11	0.4196	0.4196
	40	17.0	15.31	.0876	.0882	42.0	30.63	.2163	.2163
	50	68.0	27.62	.1890	.1892	115.0	41.44	.3196	.3198
	60	44.0	12.22	.0654	.0651	108.0	24.44	.1608	.1616
NaBr	50	10.1	25.27	0.2062	0.2060	14.30	34.49	0.2919	0.2877
	60	10.3	17.04	.1279	.1261	37.00	51.11	.4594	.4559
	70	26.1	25.04	.1984	.1975	58.5	50.09	.4448	.4453
	80	24.9	16.90	.1248	.1252	55.8	33.80	.2797	.2810
	90	36.8	16.36	.1222	.1220	59.0	40.25	.1958	.1961

Table II (continued)

Name of Substance	t	ΔP	$S \times 10^2$	$\Delta P/\Delta P_s$	S^h	ΔP	$S \times 10^2$	$\Delta P/\Delta P_s$	S^h
$K_2CO_3 . 2H_2O$	30	2 11	17.51	0.1159	0.1140	17.20	96.33	0.9495	0.9545
	40	11.10	42.74	.3470	.3465	20.00	68.38	.6252	.6226
	50	5.90	16.50	.1086	.1058	33.00	66.02	.6074	.5960
	70	14.30	15.02	.0956	.0941	80.18	60.10	.8174	.8376
	80	65.50	35.76	.2781	2775	174.0	78.68	.7387	.7415
	90	30.50	13.56	.0830	.0828	170.0	54.24	.4628	.4664
K_2CrO_4	40	2.8	37.26	0.3252	0.3196	6.2	74.70	0.7202	0.7140
	60	7.5	35.28	.3028	3003	16.6	70.58	.6700	.6689
	70	19.8	54.79	.5090	4991	37.5	95.88	.9639	.9525
	80	17.3	33.28	.2870	.2812	38.2	66.72	.6340	.6266
	90	42.8	51.94	.4649	.4692	81.3	90.87	.8833	.8956
$BaBr_2 . 2H_2O$	40	62.40	21.90	0.1504	0.1498	13.5	11.42	0.8458	0.8492
	60	15.10	40.59	.3236	.3248	25.2	16.43	.5400	.5379
	80	34.90	37.09	.2890	.2896	82.8	74.18	.6855	.6903
$ZnSO_4 . H_2O$	70	51.0	16.85	0.1681	0.1685	85.0	28.08	0.2801	0.2808
	80	10.3	23.28	.2300	.2328	12.9	29.10	.2881	.2910
	90	11.5	17.92	.1815	.1792	19.1	29.87	.2971	.2987

The experimental values of the ratio of the vapor pressure lowering and the values of S^h are given in Table II for several salts. In the second and sixth columns are given the experimental vapor pressure lowerings and in columns three and seven the corresponding degrees of saturation. The values for the vapor pressure lowerings of saturated solutions were taken from Table I. In columns four and eight are given the ratios of the vapor pressure lowerings, while in columns five and nine the corresponding values of S^h are given. Owing to the uncertainty introduced in the value of S^h by slight errors in h a more satisfactory test of this generalization is afforded by a study of the graphs of Fig. 2, rather than by an inspection of the data in Table II.

The theory as expressed by equation (10) requires that the log $(\Delta P/\Delta P_s)$ — log S graph be a straight line, and that the slope of this line be equal to h. In Fig. 2 are given such graphs for all the electrolytes for which reliable data for ΔP_s could be obtained by extrapolation of log ΔP — log S curves. The experimental values of ΔP were taken from Landolt and Börnstein's tables, and the values of S were obtained by dividing the corresponding concentration by the solubilities. It is of interest to point out that values at different temperatures were used. It is seen that the generalization is in good agreement with the data for many diverse materials.

In Fig. 3 are given the graphs of log $(\Delta P/\Delta P_s)$ against *log S*. The values of ΔP_s were experimentally determined by Bronsted[1], and the values of ΔP are those of Tammann[2]. All values are at 100°C. The interesting point about these values is the fact that ΔP_s and ΔP were experimentally determined by two different investigators, using different methods. The agreement with the requirements of the theory is a striking confirmation of Generalization 2.

Theoretical Considerations

The experimental evidence given in this paper and in the first paper confirm conclusively the relations developed. These relations, though developed empirically, must have theoretical significance because of the nature of the independent variables. No attempt, however, will be made here to formulate any theory to fit the equation. It is merely pointed out that the concentration expressed in terms of the degree of saturation leads to fundamental relations which may become important in the theory of solutions.

In connection with this, there are several relations which are interesting. The exponent h in (10) is equal to ka/b. The values for these three constants for thirty-one salts are given in the first paper.

$$K = -\left[\frac{\partial \log \Delta P}{\partial (1/T)}\right]_S$$

$$b/a = \left[\frac{\partial \log S}{\partial (1/T)}\right]_{\Delta P}$$

---

[1] Bronsted: Z. physik. Chem., **82**, 633 (1913).

[2] Tammann: Mém. Acad. Petersburg, (7) **35**, (1887); Z. physik. Chem., **2**, 42 (1888).

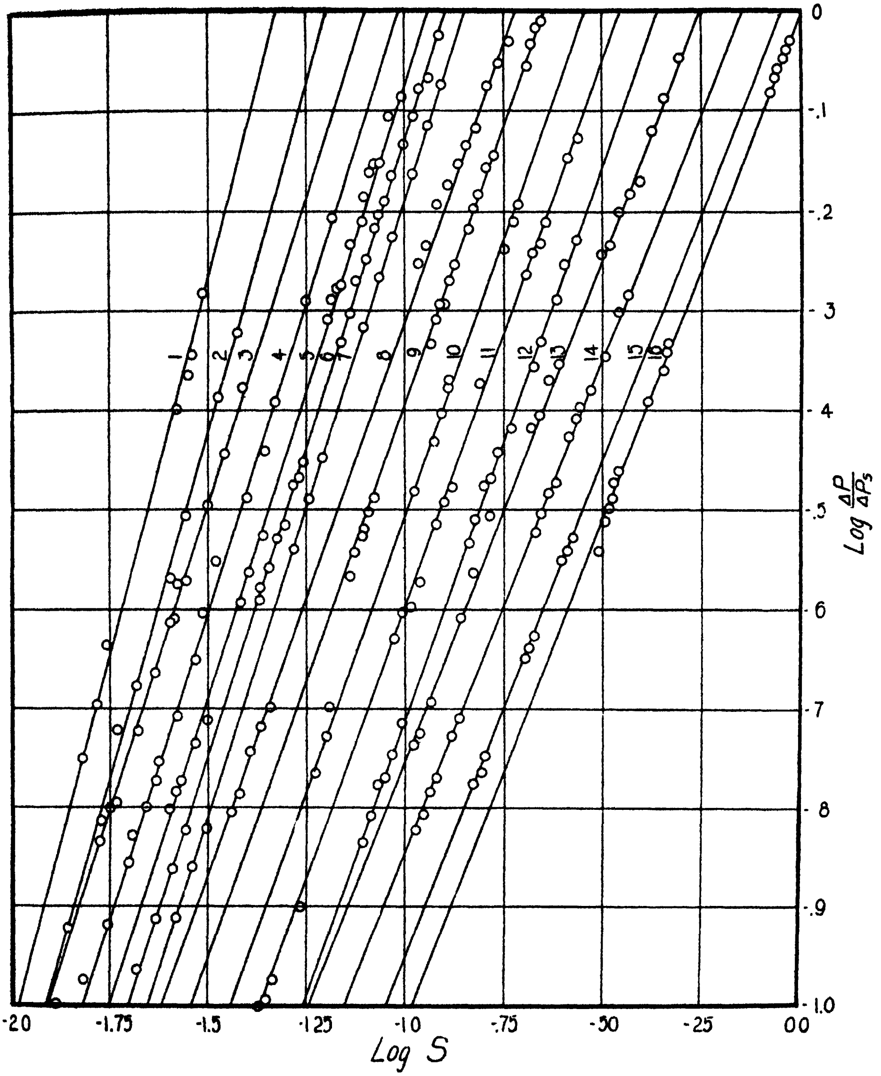


FIG. 2

$\text{Log } \frac{\Delta P}{\Delta P_s}$ – log S curves for Sixteen Salts

No. of Curve	Name of Substance	Log S Scale	No. of Curve	Name of Substance	Log S Scale
1	$MgCl_2$	Add 1.30	9	K_2CrO_4	Add 0.65
2	$SrBr_2$	" 1.20	10	Na_2CO_3	" 0.58
3	$SrCl_2$	" 1.12	11	RbCl	" 0.45
4	NaI	" 1.00	12	KI	" 0.35
5	LiCl	" 0.45	13	KCl	" 0.25
6	K_2CO_3	" 0.90	14	$(NH_4)_2SO_4$	" 0.15
7	$BaBr_2$	" 0.85	15	$ZnSO_4$	" 0.05
8	$BaCl_2$	" 0.70	16	Na_2SO_4	" 0.00

but

$$-\left[\frac{\partial \operatorname{Log} \Delta P}{\partial (1/T)}\right]_S \Big/ \left[\frac{\partial \log S}{\partial (1/T)}\right]_{\Delta P} = \left[\frac{\partial \operatorname{Log} \Delta P}{\partial \log S}\right]_T$$

therefore

$$\left[\frac{\partial \operatorname{Log} \Delta P}{\partial \log S}\right]_T = Ka/b = h$$

The values of *h* are given in Table III. It will be seen that the electrolytes can be divided into three classes, namely

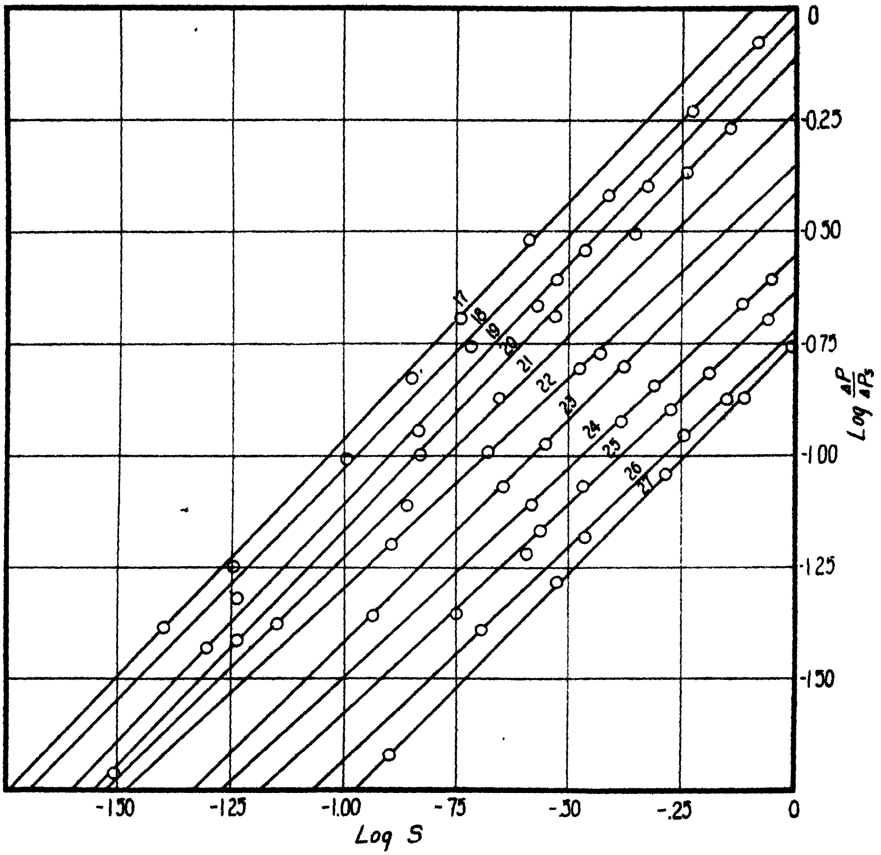


Fig. 3

Log S–log $\frac{\Delta P}{\Delta P_s}$ curves for salts for which datad ΔP_s are available at 100°C

No. of Curve	Name of Substance	Log P/ΔP_s Scale	No. of Curve	Name of Substance	Log P/ΔP_s Scale
17	NaBr	Subtr. 0.10	23	$NaClO_3$	Add 0.55
18	KBr	Add 0.00	24	K_2SO_4	” 0.25
19	KI	” 0.10	25	$KClO_3$	” 0.65
20	NaCl	” 0.10	26	KCl	” 0.70
21	KNO_3	” 0.50	27	Na_2SO_4	” 0.75
22	$NaNO_3$	” 0.45			

TABLE III

Values of the Exponent h

Name of Substance	h		Name of Substance	h	
$NaNO_3$	0.8412	group I	$NaI \cdot 2H_2O$	1.143	group IIIb
KNO_3	.8933		$LiBr \cdot 2H_2O$	1.152	
NH_4Cl	.8950		K_2CrO_4	1.155	
$ZnSO_4 . H_2O$	.9971	group II	$NaClO_3$	1.205	
Na_2SO_4	.9976		$BaBr_2 \cdot 2H_2O$	1.240	
$(NH_4)_2SO_4$	1.000		$K_2CO_3 \cdot 2H_2O$	1.252	
$ZnSO_4 . 6H_2O$	1.000		$LiBr \cdot H_2O$	1.256	
KCl	1.000		$NaBr \cdot H_2O$	1.263	
NH_4Br	1.033	group IIIa	$LiCl$	1.263	
$Na_2CO_3 \cdot 2H_2O$	1.037		$SrCl_2 \cdot 6H_2O$	1.307	
$NaBr \cdot 2H_2O$	1.049		$CaCl_2 \cdot 2H_2O$	1.317	
$NaCl$	1.049		$SrBr_2 \cdot 6H_2O$	1.323	
KBr	1.060		$MgCl_2 \cdot 6H_2O$	1.403	
$RbCl$	1.094		$NiSO_4 \cdot 6H_2O$	1.559	
$BaCl_2 \cdot 2H_2O$	1.109		$CoSO_4 \cdot 7H_2O$	1.670	
KI	1.138		$Be_2(SO_4)_3 \cdot 4H_2O$	1.698	

(1) $h < 1$; (2) $h = 1$; (3) $h \triangle 1$.

Now, when $\triangle P$ is plotted against S characteristic curves are obtained for each group. Where h equals 1, these curves are straight lines. The curves for $(NH_4)_2SO_4$ are shown in Fig. 4a. Where h is less than one, the curves are concave downward. In Fig. 4d are shown such curves for $NaNO_3$. For substances for which h is greater than 1 two modifications exist, as shown in Fig. 4b and 4c. The former are concave upward till a certain degree of saturation is reached, when they become straight lines, while the latter are concave upward continuously. The examples given are $BaCl_2$ and LiCl. Whatever the theoretical significances of these curves may be, they are probably indicative of the molecular constitution of the solution.

Conclusion

The degree of saturation is the ratio of the number of moles of solute dissolved in a given quantity of solvent to the number of moles of solute that this given quantity of solvent can hold in solution under similar conditions.

The theoretical significance of this ratio is of prime importance when the molecular conditions of an under-saturated and saturated solutions are identical. This is obviously, not the case when the usual solubilities are used inasmuch as the solubility as generally determined is affected both by "self-salting out" as well as adsorption.

Various theories have been suggested to explain the salting-out effect[1]. Whatever the real explanation may be, it is certain that the presence of solute molecules or ions affects the power of the solvent to dissolve. This, no doubt is true when only one kind of solute is present as well as when a second solute is present. This effect is what is termed in this paper and in the preceding paper "self salting-out".

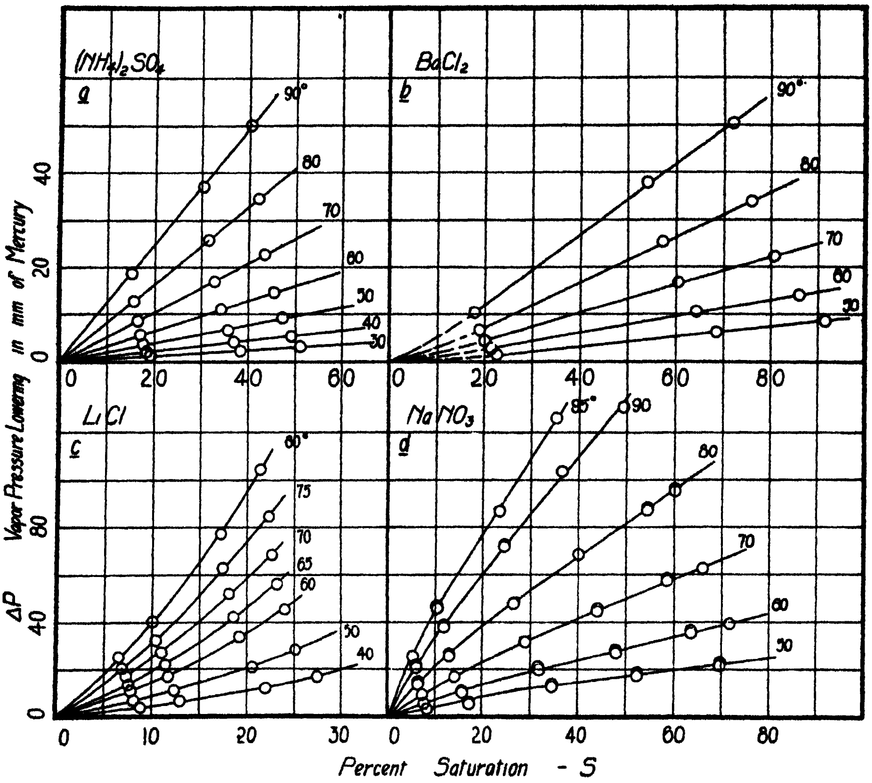


FIG. 4
Typical ΔP-S Curves

It has long been known that salt crystals strongly adsorb a common ion from solution. While this has been appreciated analytically the most convincing evidence has come from the study of the electric charges carried by colloidal particles of insoluble salts. In a recent investigation Fajans and Frankenburger[2] have determined the amount of adsorption of silver ions by silver bromide crystals. Solubility is the concentration of the liquid phase in equilibrium with the solid phase. Solubility so defined must be corrected for adsorption as well as "self-salting" out in order to obtain the "real" solubility. The degree of saturation expressed in terms of this "real" solubility will be different from the degree of saturation used in these papers. We should expect therefore, regular deviations from the relations developed here. These deviations are probably negligible or at any rate are masked by the experimental error. If more accurate date should become available, this deviation will no doubt become apparent. This, however, does not invalidate the relations developed nor does it vitiate the importance of the concept of the degree of saturation.

---

[1] Euler: Z. physik. Chem., **31**, 360 (1899); Geffcken: **49**, 257 (1904); Levin: **55**, 503 (1906); Rothmund: **33**, 401 (1900); **69**, 523 (1909); Lowry: Trans. Faraday Soc., **1**, 197 (1905); Philip: J. Chem. Soc., **91**, 711 (1907); McKoawn: J. Am. Chem. Soc., **44**, 1203 (1922).

A thorough discussion and resumé of this subject is given in the American adaptation of Eucken, Jette and LaMer, loc. cit. (p. 341-348).

[2] Z. physik. Chem., **105**, 255 (1923).

Summary

In this paper additional experimental proof was given in confirmation of the two generalizations:—

Generalization 1:—The ratio of the vapor pressure lowering ΔP at any degree of saturation and the vapor pressure lowering of a saturated solution ΔP_s is independent of the temperature.

Generalization 2:—The ratio $\Delta P/\Delta P_s$ is a simple function of the degree of saturation, i.e.

$$\Delta P/\Delta P_s = S^h$$

where

$$h = Ka/b = \left[\frac{\partial \log \Delta P}{\partial \log S}\right]$$

These two generalizations are deducible directly from an equation developed in a previous paper which connects the vapor pressure lowering with the degree of saturation. The equation is

$$\log \Delta P = K\,[1/T - a\,(1 - \log S/b)]$$

where K, a, and b are constants, S the degree of saturation, ΔP the vapor pressure lowering, and T the absolute temperature.

Havemeyer Chemical Laboratory,
New York University,
New York City.

THE PREPARATION AND CONDITIONS OF FORMATION OF THE TWO POSSIBLE TYPES OF EMULSION IN THE SYSTEM CRESYLIC ACID—GELATINE—WATER*

BY ROWLAND MARCUS WOODMAN

It is the belief at present that an emulsifier is capable of promoting the one type of emulsion only with any two given liquids[1].

Weston[2] investigated the efficiency of colloidal clay as an emulsifier of oils and fats, and makes a statement that colloidal clay is capable of facilitating the emulsification of oil in water or of water in oil.

During some work on emulsions, with a view to their application to trees as contact insecticides[3], it was found that certain mixtures of soft soap, cresylic acid, and paraffin oil were completely soluble in water, provided the water were present in excess of a definite amount depending on the relative proportions of soap, cresylic acid and paraffin oil. If the water were below this amount, mixtures of solutions and emulsions were formed; both types of emulsion were suspected, according to the amounts of water added, but, as the system was so complicated, this could not be proved. It was resolved, therefore, to choose some simpler analogous system which would offer every facility for the formation of the two types of emulsion, if these were at all possible.

The system chosen consisted of the two liquids water and "cresylic acid" (a mixture of the three cresols labelled "pure"), the emulsifiers being gelatine (Coignet's Gold Leaf Label, and the same purified by a modification of Loeb's process[4]). The advantages of this system are obvious: gelatine gives a colloidal solution with water and is soluble[5] in cresylic acid; if the type of emulsion formed in a system is conditioned by the fact that the future external phase liquid wets the emulsifier, then the chosen system should, by altering the conditions of experiment, favor both liquids in turn. For in view of the fact that an aqueous gelatine solution forms the continuous phase of many emulsions, water must, on the above hypothesis, wet the particles of gelatine in an aqueous colloidal solution of gelatine; on the other hand, if gelatine dissolves in cresylic acid, it is justifiable to assume that the solute is wetted by the solvent. Hence, in the chosen system, where the gelatine is capable of being wetted by both liquid phases (as shown by simply dipping gelatine into the two liquids), it may be possible to form both types of emulsions by varying the conditions.

Experimental: 0.4% solutions of pure gelatine were made in distilled water, and in cresylic acid.

---

* School of Agriculture, University of Cambridge.

[1] Clayton: "Emulsions and Emulsification", 7 (1923).

[2] Weston: Chemical Age, 4, 604, 638, 640 (1921).

[3] Woodman: J. Pomology and Horticultural Science, 5, 43 (1925).

[4] Loeb: "Proteins and the Theory of Colloidal Behaviour", (1922).

[5] Stocke: "Brit. Ass. Colloid Reports", 1, 74 (1917).

The first experiments were made to ascertain (assuming the two types of emulsion possible), if the type formed depended on previous wetting of the emulsifier by one of the liquid phases: definite volumes of aqueous gelatine and cresylic acid, and of distilled water and cresylic acid gelatine solution, were shaken together in stoppered graduated 50 c.c. cylinders and left to cream[1]. The results obtained are given in Table I.

TABLE I

1 c.c. of 0.4% aqueous gelatine	2 c.c. of cresylic acid	3 c.c. of 0.4% cresylic acid gelatine	4 c.c. of Water	5 c.c. of B	6 c.c. and character of cream	7 Description of emulsion from Drop Test on cream	8 % by vol. of disperse phase in cream on basis of full creaming	9 % by vol. of disperse phase obtained by cracking known vol. of cream
10	—	—	—	10	13 u	W in B	76.92	—
25 (1%)	—	—	—	5	s	B " W	—	—
20	—	—	—	10	14 s	B " W	71.43	70 of B
25 (1%)	5	—	—	—	u	C " W	—	—
30	5	—	—	—	7 u	C " W	71.43	—
25	2	—	—	—	u	C " W	—	—
200	30	—	—	—	38 u	C " W	78.94	63.63 of C
—	—	200	30	—	s	W " C	—	—
30	5	—	—	—	u	C " W	—	—
30	10	—	—	—	u	C " W	—	—
30	15	—	—	—	u	C " W	—	—
20	15	—	—	—	u	C " W	—	—
10	10	—	—	—	u	C " W	—	—
10	15	—	—	—	u	C " W	—	—
10	20	—	—	—	s	W " C ↓	—	—
—	—	30	5	—	s	W " C	—	—
—	—	30	15	—	s	W " C	—	28 of C.
—	—	10	10	—	u	C " W	—	—
—	—	10	15	—	u	C " W	—	—
—	—	10	20	—	u	C " W ↓	—	—
32	10	—	—	—	u	C " W	—	—
10	10	—	—	—	s	W " C	—	—

Notes on Table I.

Column 5. B is a mixture (1.1 by volume) of toluene and cresylic acid and is less dense than water; W = water; C = cresylic acid.

Column 6. Shows the volume of "cream" when the emulsion is apparently fully creamed (3 b); *s* means a supernatant cream; *u* that the cream tends to settle to the bottom.

---

[1] Woodman: J. Pomology and Horticultural Science", 4, 184 (1925).

Column 7. Indicator methods were not of much use in determining the type of emulsion formed, as cresylic acid and water are mutually miscible to some extent. The drop test was found quite applicable, especially when carried out on the creams. The types were also recognizable by their behaviour in a wet pipette, the W in C cream forming a film, difficultly removable by running water, on pipetting up and running out of the pipette. A further differentiation of the two types was afforded by the method of creaming: thus a B in W emulsion creams normally whilst a W in B emulsion tends to "cream" downwards to form an "undercream"; C in W emulsions form undercreams and W in C emulsions ordinary creams. The method of creaming is thus obviously correlated with the densities of the two liquid phases and the type of emulsion formed.

Column 8. Assuming that the disperse phase of an emulsion consists of small spheres of the same diameter, the closest packing of the spheres (without distortion), allows 74% of the space occupied to consist of disperse phase. This fact has been applied to emulsion creams (6), and it has been shown experimentally that complete creaming of emulsion mixtures results in the formation of a cream containing approximately the mathematical limit 74% by volume of disperse phase (*e.g.*, for 32 observations[1] the average was 72.28 ± 0.67). This allows two further methods of determining the type of emulsion formed. In the first place, assuming all the disperse phase to be in the cream (which is usually the case for simple one-type systems such as oil—emulsifier—water, where the oil and water are immiscible and the oil is not soluble to any appreciable extent in the continuous medium[2], measurement of the final volume of cream (which is usually well-defined[3]), (6 and 3 b), obtained by shaking known unequal volumes of the two liquid media with emulsifier, allows calculation of the volume percentages in the cream of either liquid, assuming each in turn to be the disperse phase, and that complete emulsification of one liquid has taken place. That percentage which comes within the approximate range 65—80 is then likely to be that of the internal phase liquid, being nearer to the theoretical 74%. In the case where the phase liquids have very different volumes (e.g. 2: 1 or 3: 1), no calculation is necessary, for the volumes of cream widely differ for the two types.

This method was found to be of little use in the present system, as the C in W emulsions were usually unstable, free cresylic acid being present in nearly every case; it was applicable, however, to most emulsions of the opposite type.

Column 9. Illustrates the second method of differentiation by means of the emulsion cream, and consists in "cracking" a known volume of the cream obtained after complete creaming, by adding a concentrated acid (hydrochloric, which has not tendency to react with the cresylic acid), and, after waiting a few days, reading off the volume of cresylic acid obtained. If the volume of cresols approximates to 74% of the cream taken, the emulsion is C in W; if to 26%, then it is W in C. This method was found applicable, as was the first, to most W in C emulsion creams, but failed with most C in W emulsions, apparently because these "broke" long before complete creaming was possible.

---

[1] Woodman: J. Pomology and Horticultural Science, **4**, 184 (1925).

[2] Pickering: J. Chem. Soc., **111**, 86 (1917); Woodman: l. c.

[3] Pickering: J. Chem. Soc., **91**, 2001 (1907); Woodman: l. c.

Discussion of Results of Table I

Table I shows that, in the given system, it is quite possible to make the two types of emulsion. Apparently the previous suspension or solution of the emulsifier in one of the liquids does not appear to determine the type of emulsion subsequently formed. Experiments on another system bore this out: a clean cork was filed and ground to a fine state of division, and the cork dust ground with water. The larger particles floated to the surface, leaving an aqueous suspension of very fine cork dust underneath, the dust presumably being wetted by the water. Ten c.c. of this suspension were pipetted off and shaken with 10 c.c. of toluene. A comparatively stable emulsion resulted, which rapidly creamed on standing. The cream finally possessed a volume 12.4 c.c. (*i.e.* 80.65 per cent. of disperse phase, assuming no miscibility of the two media). As the cream rose to the surface, was capable of dilution by water, and as the globules became dark red on dusting a little Sudan III over the surface and shaking, the emulsion was of the oil in water type.

Twenty c.c. of a similarly formed suspension of fine cork dust in toluene were now shaken with 20 c.c. of water. A creamy-looking emulsion resulted, which creamed normally and very quickly, giving 24.75 c.c. of cream, *i.e.* 80.79% of disperse phase. Similar tests to those above proved the emulsion to be of the oil in water type also, though one might assume previous thorough wetting of the emulsifier—cork dust—by the toluene. The emulsion was very unstable, the cream rapidly becoming coarse-grained in character.

The results of these two experiments, together with those of Table I, tend to show that previous wetting of the emulsifier by suspension in one of the liquids is no criterion of the type of emulsion subsequently formed. It must be borne in mind, however, that toluene might exert considerable solvent action on portions of the cork, the emulsifier thus being different (and not a mere suspension of small solid particles of cork), in the two cited cases. A water film might also conceivably replace the toluene film round the cork in the second case, thus explaining the instability noticed; for whereas toluene can replace a water film on a solid surface in a few minutes, water may take weeks to replace entirely a film of an immiscible organic liquid such as toluene[1]. The formation of the same type of emulsion in both experiments would, on the hypothesis of replaceable films, in conjunction with the usual theory of emulsification, have to be put down to a *preferential* wetting of the cork by water.

Table I shows clearly that the relative volumes of the liquid media have a great effect on the type of emulsion formed. Thus a large relative amount of aqueous phase predisposes to the C in W type, and vice-versa, irrespective as

---

[1] Reynolds: J. Chem. Soc., 119, 460 (1921).

Table II

10 c.c. aq. solution of pure gelatine.
10 c.c. cresylic acid.

No. of Expt.	Method of Treatment	Type of Emulsion Formed	c.c. and character of cream	% by vol. of disperse phase in cream on basis of full creaming
1	Preliminary 10 min. standing before shaking	C in W	u	—
2*	Immediate continuous shaking	W in C	s	—
3†	Stand 15 min. first, then gentle partial rotation before shaking.	C in W	u	—
4*	Stand 30 min., then continuous shaking	W in C	12.5 s	80.00
5*	Stand 40 min. and then intermittent shaking at rate of one shake per 30 sec.	W in C	13 s	76.92
6	Intermittent shaking at rate of one shake per 30 sec.	C in W	u	—
7*	Intermittent shaking at rate of one shake per sec.	W in C	13 s	76.92
8*	Immediate continuous shaking	W in C	s	—
9	Pipette acid into aq. phase in stream of small drops; gentle partial rotation for a min., and then intermittent shaking—1 per sec.	C in W	u	—
10	Intermittent shaking—1 per 30 sec.	C in W	u	—
11*	Immediate continuous shaking	W in C	12.75 s	78.43
12	Gentle partial rotation and then continuous shaking	C in W	u	—
13*	Four intermittent shakes—1 per 30 sec.	W in C	12 s	83.33
14*	(0.3%) Two intermittent shakes —1 per 30 sec.	W in C	12 s	83.33
15	Gentle partial rotation and then intermittent shaking	C in W	u	—
16	Gentle partial rotation and then continuous shaking	C in W	u	—
17*	Immediate continuous shaking	W in C	12.5 s	80.00
18	One very feeble shake and then vigorous intermittent shaking at rate of 1 shake per 30 sec.	C in W	u	—
19	One very feeble shake—wait 30 sec.—then vigorous continuous shaking	C in W	u	—

to which phase first contains the emulsifier. The ranges of results 9 to 15 and 16 to 20, marked by arrows, clearly demonstrate this fact.

Finally, Table I indicates the fact that, in one case, where the same absolute proportions of the two liquids and of the emulsifier are present (results 13, 22 and 18), the two types of emulsion are possible. As no records of the exact methods of preparation of the emulsions in Table I were noted, it was thought necessary to make further experiments to determine the conditions governing the formation of the two types of emulsions in the above special cases.

Conditions of Formation of the Two Types of Emulsion when the Constituents of the System are always present in the Same Amounts

In the following experiments, ten c.c. of a 0.4% aqueous solution of pure gelatine were shaken with ten c.c. of cresylic acid, the same stoppered cylinder being used in every case. Except where stated otherwise, the aqueous phase was pipetted very slowly and carefully down the cylinder's side to the surface of the cresylic acid, without disturbing the acid. The cylinder's contents were, in different cases, subjected to different treatments previous to emulsification. The results are given in Table II.

Notes on Table II

The asterisk indicates a W in C emulsion; it was found, in all such cases, that, on shaking, the emulsion wetted the sides of the cylinder to form a continuous film, which ran down to the main body of emulsion, the film draining thinner, without actually breaking, during a considerable period. The W in C type was comparatively slow-creaming, two or three days being necessary for full creaming; the cream rose, as the disperse phase (water), was less dense than the continuous medium. The creams, moreover, were stable, showing little tendency to break; measurement of the volume of the cream, and cracking of the cream, therefore, gave good indications as to the amount and identity of disperse phase.

The emulsions not so marked were of the opposite type and showed different behaviour: on shaking and standing, the film on the cylinder immediately broke and ran up into drops. In few cases (to be quoted later), and then, apparently fortuitously, was all the cresylic acid emulsified, a few drops generally collecting at the surface of the emulsion, most of these drops falling subsequently. The emulsion mixtures started creaming practically immediately, the cream collecting at the bottom (the disperse phase, cresylic acid, being denser than the aqueous continuous medium). The emulsions were unstable and showed great tendency to crack even whilst creaming, a period of six hours to two days usually completing the cracking; this behaviour was probably due to the unemulsified cresylic acid present, and it meant that volume measurements and cracking of the cream did not give reliable data regarding the disperse phase; occasionally, however, the emulsions were stable a sufficient length of time to allow of such data (e.g. Table I, result 7). After an hour or so, the C in W emulsions usually presented the following appearance: a thin layer of cresylic acid (unemulsified or got by cracking of the emulsion), surmounted by a layer of cream, in turn surmounted by a layer of excess aqueous continuous phase with a drop of cresylic acid at the center of the free surface. The under-creaming and drop test were taken as criteria of the type.

In one case (result 18) the C in W emulsion appeared stable, the emulsion settling slowly to a layer of cream surmounted by excess aqueous phase, no layer of free cresols being present. No. 15 also appeared moderately stable. Both of these, on reshaking, gave emulsions stable enough to allow readings of the volumes of cream, though they were now slow-creaming, as with the W in C type. In both cases there were 14½ c.c. of undercream surmounted by 5½ c.c. of clear aqueous layer, the percentage of disperse phase thus being 68.96. Twenty c.c. of a mixture containing equal volumes of both creams gave, on cracking with 20 c.c. concentrated hydrochloric acid and waiting two or three days for complete separation, 11.75 c.c. (i.e. 58.75%) of cresylic acid, showing the cream to be of the C in W type.

5 c.c. of the cream from each of eight W in C emulsions (i.e. 40 c.c. total), were mixed and cracked with 40 c.c. of concentrated hydrochloric acid; after waiting a few days to ensure complete separation, 13 c.c. of cresylic acid (i.e. 32.5%) were obtained, showing the acid to be the external phase.

It is noteworthy that when any C in W emulsion completely and spontaneously cracked on standing, subsequent reshaking by any method always re-formed the C in W emulsion.

The dagger (Exp. 3) indicates gentle partial rotation. The stoppered cylinder was grasped at each end and gently rotated until its major axis was horizontal; the cylinder was then slowly and gently rotated in a vertical plane backwards and forwards through about 2°, the centre of the major axis acting as a pivot, for at least a minute.

Discussion of Table II

Results 1 and 2 seem to point to the fact that the period of standing previous to shaking determines the type formed; evidently these results were fortuitous, for results 4, 5 and others proved this hypothesis to be false. Results 3 and 4 tend to show that the formation of the two types is due to the method of treatment previous to shaking. Results 6 and 10 tend to point to the fact that intermittent shaking gives the C in W type. The results were fortuitous, subsequent experiments disproving them; possibly the intermittent shaking was very gentle.

The later experiments were designed to show the effect of vigour of shaking; it will be seen that, in the main, immediate vigorous shaking *e.g.* ordinary continuous or intermittent shaking by hand) gives the W in C type, whilst a preliminary gentle treatment—either by gentle rotation or very gentle shaking—followed later by *any* method of shaking, gives the C in W type.

Influence of temperature on formation of types:

In no circumstances tried could the C in W type be prepaied at 52°C. when the proportions used were 10 c.c. of 0.4% aqueous gelatine to 10 c.c. of cresylic acid.

Repetition of Experiments using a cresylic acid solution of gelatine:

The previous experiments were repeated using a 0.4% solution of gelatine in cresylic acid, and water. The two liquid media were used in different proportions, two experiments in which the methods of shaking were different being done for each proportion. The results are given in Table III.

TABLE III

c.c. Water	c.c. 0.4% cresylic acid gelatine	Method of Treatment	Type of Cream	Type of Emulsion by Drop Test
20	5	Gentle partial rotation previous continuous shaking	u	C in W
20	5	Vigorous continuous shaking	u	C " W
10	5	do. to 1	u	C " W
10	5	do. to 2	u	C " W
10	10	do. to 1	u	C " W
10	10	do. to 2	u	C " W
5	10	do. to 1	u	C " W
5	10	do. to 2	s	W " C
5	15	do. to 1	s	W " C
5	15	do. to 2	s	W " C

The results indicate that the previous solution of gelatine in the cresylic acid has not much effect on the general trend of the results of the experiments previously carried out. If the cresylic acid is in excess, the W in C type is formed (results 9 and 10), and if the water is in excess (results 1-6), the C in W type is formed, irrespective of the mode of treatment. Results 5 and 6 (agreeing with result 18, Table I show that equal proportions of the two phases give the C in W type irrespective of treatment, the proportions which yield the two types by different treatment now being 5 of water to 10 of cresylic acid gelatine.

Table IV is a collection of results bearing out the whole of the findings previously discussed; results 16-28 were got when using aqueous commercial gelatine solutions (0.4% except when stated otherwise) and results 22-28 when using another sample of cresylic acid (B.D.H. pure). It will be seen that the different samples of cresylic acid give the same results, and that the presence of traces of inorganic constituents in the commercial gelatine apparently had no effect. The commercial gelatine contained 20% of water approximately, the pure sample of the same being anhydrous.

Continuous shaking means ordinary (vigorous) hand shaking.

It will be seen that an excess of one of the liquid phases causes that phase to become the external one (results 1-16); two proportions gave the dual types of emulsions by different methods of treatment (results 5-14), immediate vigorous shaking giving the stable W in C type, and preliminary gentle partial rotation, or very gentle shaking, giving the C in W type (results 17-28).

It was noticed that, where the dual types could exist for a certain proportion of liquid phases, the resulting type for a definite mode of shaking could be predicted if the gelatine solution were at least a day old.

TABLE IV

c.c. 0.4% aqueous gelatine	c.c. cresylic acid	Method of Treatment	Type of cream	Type of Emulsion by Drop Test
30	15	Continuous shaking	u	C in W
30	15	Gentle partial rotation then continuous shaking	u	C " W
20	15	Continuous shaking	u	C " W
20	15	Gentle partial rotation then gentle shaking	u	C " W
10	10	Continuous shaking	s	W " C
10	10	do.	s	W " C
10	10	Gentle partial rotation then continuous shaking	u	C " W
10	10	do.	u	C " W
10	10	Very gentle shake—wait 30 sec.—continuous shaking	u	C " W
10	10	do.	u	C " W
10	10	Continuous shaking	s	W " C
10	10	Gentle partial rotation then continuous shaking	u	C " W
10	15	Continuous shaking	s	W " C
10	15	Very gentle partial rotation then gentle shaking	u	C " W
10	20	do.	s	W " C
10	20	Continuous shaking	s	W " C
20 (1%)	10	Gentle partial rotation then continuous shaking	u	C " W
40 (1%)	10	do.	u	C " W
150 (1%)	10	do.	u	C " W
10	10	Continuous shaking	s	W " C
10	10	Gentle partial rotation then continuous shaking	u	C " W
10	10	*Very gentle* continuous shaking	u	C " W
10	10	do.	u	C " W
10	10	Continuous shaking	s	W " C
10	10	do.	s	W " C
10	10	do.	s	W " C
10	10	Gentle partial rotation then continuous shaking	u	C " W
10	10	*Very gentle* continuous shaking	u	C " W

In Table IV total emulsification of cresylic acid was never obtained, and hence the C in W emulsions were unstable and cracked spontaneously in a period varying from a few hours to a day or so. Subsequent shaking by any method tried always gave the C in W type again, the second emulsion, got in this way, seeming more stable and lasting than the first.

On trying to repeat the experiments with a two-months' old solution of the commercial gelatine (putridity having been prevented by adding a little toluene when the solution was a few days old), it was found that the C in W type of emulsion only could be prepared, however vigorous the shaking given to the system. Two of the C in W emulsions prepared from this old solution were very stable, the undercreams taking about two days to form fully (slow creaming was found to be a sign of complete, or practically complete, emulsification, thus connoting stability). Measurement of the volumes of the undercreams thus allowed estimation of the percentage of disperse phase (77% in both cases), assuming complete emulsification. The undercreams were like sediments of a solid in an extremely fine state of division, and had not the translucent, slightly oily appearance of the supernatant W in C creams.

Two factors, the added traces of toluene, and the age of the gelatine solution, might have accounted for the above phenomenon. It has already been observed, with regard to the second factor, that, with solutions of gelatine less than a day old, difficulty was experienced in forecasting the type of emulsion resultant upon a particular mode of shaking (extraordinary care had to be taken to make the C in W type), and hence the age of the solution apparently exerts a great effect.

The importance of both these factors was tested; a 0.4% solution of commercial gelatine was made, and traces of toluene were added to prevent putrefaction. The types of emulsion possible by all methods of shaking were then noted for the gelatine solution at different ages. At the same time, the

TABLE V

10 c.c. of 0.4% aq. gelatine solution.
10 c.c. of other phase.

Age of Gelatine Solution reckoned from Time of Making (h.r)	Other Liquid Phase	Temp.	Types of Emulsion found possible by *any* method of Hand-shaking
2	Cresylic acid	room	W in C; C in W
24	do.	do.	W in C; C in W
49	do.	do.	W in C; C in W
50-51	o-cresol	do.	W in o-C; o-C in W
50-51	m-cresol	do.	W in m-C; m-C in W
50-51	p-cresol	do.	W in p-C; p-C in W (stable)
168-170	cresylic acid	do.	W in C (*very* unstable); C in W
336	do.	do.	C in W only
336-338	do.	52°C	W in C (*very* unstable) only

possibility of the formation of both types when using pure o-, m- and p-cresols[1], instead of the cresylic acid, was tested. The effect of temperature on the type formed was also repeated. The results are given in Table V.

The W in C, o-C, m-C or p-C were always stable, giving measurable supernatant creams, except where stated otherwise; the reverse types, except p-C in W, usually were of the type already described, i.e. took a few hours at least to break completely.

The newest solution used was two hours old, as a certain time had to be given to allow the solution to cool to room temperature; with this solution, as with other ones, both types of emulsion were possible, and hence, in this respect at least, the effect of traces of toluene can be neglected.

When the phases were heated to 52° previous to emulsification, the W in C type was the only one possible, agreeing with previous results. If heating a gelatine solution is regarded as a reversal of the ageing effect[2], destruction of the solid network taking place, then the above fact, taken in conjunction with the previously observed tendency of a new gelatine solution to form W in C emulsions—the reverse type being hard to prepare—points to the conclusion that a cool new solution (age = 0 hr.) of gelatine would probably form the W in C type only.

Older solutions of gelatine (170 hr.) still form both types, the W in C type, however, being very unstable and completely breaking in about 15 minutes; with older solutions still (366 hr.), the C in W type alone is possible at ordinary temperatures.

The older solutions did not, in the present instance, give stabler C in W emulsions; this might be correlated with the fact that the gelatine was subjected to hydrolysis even though toluene was present, the solution obviously having a maximum viscosity at about 2-4 days old. (*N.B.* it has been shown that a solution of pure gelatine attains and keeps a maximum viscosity, and does not show signs of putrescence, owing probably to lack of ash[3]; a gel (previously boiled), of the pure gelatine used in the present experiments, inoculated with liquefying bacteria, showed scarcely a trace of their presence after a month[4]. The reason for using commercial gelatine in these last experiments (and hence having to preserve with toluene) was lack of pure sample).

These later results also showed the impossibility of absolutely standardizing the methods of preparation of the two types, for *very* vigorous shaking was found to be necessary to form the water in cresylic acid (or cresol) type. This shaking was given by means of vigorous (and long), shakes, the whole arm from the elbow down taking part, the wrists being stiff. Shaking from the wrist merely (short shakes), however vigorous, gave the reverse type.

---

[1] Kahlbaum's cresols (liquefied first), kindly provided by F. C. Thompson, Esq., M.Sc., of the Procter Research Laboratory, Leeds.

[2] Woodman: Unpublished data.

[3] Woodman: J. Pomology and Horticultural Science, 4, 95 (1925).

[4] This test was kindly done for me by Mr. H. P. Hale, of the Low Temperature Research Station, Cambridge.

This might be different behaviour from that noticed before (where very gentle shaking was necessary to give the C in W type), or it might be a point previously overlooked.

In some cases tried it was found that reshaking an old creamed W in C emulsion mixture where the proportions of phases were such as to make both types possible, caused reversion to the C in W type; re-shaking a broken or partially broken C in W emulsion mixture by any method also always gave a C in W type.

The results with commercial gelatine as emulsifier were not so trustworthy and standard as those obtained by using pure gelatine.

General Discussion of Results

An explanation of the formation of the two types of emulsion in the cases quoted is difficult: there are many possible factors to be taken into account, *e.g.*, the relative wetting powers of the two liquid phases for the emulsifier (consideration of surface forces), the possible formation of gelatine cresate or cresates, the partition of gelatine between water and the cresols, the possible non-emulsifiability of one or more cresols, the size of gelatine particles in the two liquid phases, the ageing of solutions and, obviously, the method of preparation, *etc.*

The partial emulsification of o- and m-cresols and the total emulsification of p-cresol point to the fact that, in the case of cresylic acid, no definite cresol remains wholly unemulsified.

The influence of the formation of gelatine cresates or cresate on the type formed cannot be great, for it will be observed that both types can be prepared in certain cases, by altering the mode of shaking, whether the gelatine be first dissolved in the cresylic acid (a condition which should favor formation of cresates) or in the water. The same experiments show that previous wetting of the emulsifier (and, therefore, interfacial forces) by one of the liquid phases, has little apparent effect.

The method of shaking is obviously, in the cases quoted, of great importance in determining the type formed; a tentative, but by no means a definite explanation is given below, taking this fact into account.

In the first place it will be postulated that colloidal solutions may be of two kinds: (a), where the solute molecule is so large as to make the solution colloidal, and (b), where simple (or complex), molecules are in such a state of aggregation as to make the disperse phase particles colloidal in size. Now it is stated that gelatine is soluble in cresylic acid (*loc. cit.*), presumably to give a true solution; but a cresylic acid solution of gelatine has been proved to be capable of forming the external phase of an emulsion, contrary to the general experience, that an emulsifier is usually, in the limit, in a colloidal state of division, and not more finely-divided. It is probably better to assume that the solution of gelatine in cresylic acid is rather colloidal (possibly due to factor (a) above), than true; then the most that can be stated is—even this is contrary to general experience—that an emulsion can be formed when the emulsifier is capable of forming some type of solution with *both* liquid phases.

As the emulsifier is "soluble" in both liquid phases, there must be some kind of partition coefficient existing between the two liquids. An explanation of the formation of the W in C type by means of vigorous shaking (sometimes only one shake is necessary), whether the gelatine is first dissolved in the cresylic acid or the water, can be based on this notion: a vigorous shake breaks up both liquid phases momentarily into very small droplets, the two liquids being thrown into close juxtaposition; the partition of gelatine then takes place rapidly (possibly hastened by the greater solvent action of small drops), and, because the particles of gelatine in the cresylic acid are probably smaller and much more numerous than in the water, they are adsorbed on the water globules, the cresylic acid coalescing to form the external phase.

In the case of the C in W type the gentle shaking or previous partial rotation does not break the phases into very small droplets (it was noticed that in the case of cresylic acid rotated with aqueous gelatine, the acid not only tended to break, and then into coarse globules), and hence partition of the gelatine is made difficult. Now there is good evidence for believing that a time factor is concerned in the formation, or completion of formation, of the adsorbed layer at the dineric interface of emulsions, (cf. Briggs's work on the value of intermittent shaking[1] and Nugent's work on the inhibition period in the formation of emulsions[2]). An alternative explanation to that provided by Briggs as regards the value of intermittent shaking in formation of emulsions has been given[3]: a time factor has been assumed so that any adsorption at the interface, following a shake, is firmly established if there is a period of waiting before the next shake; continuous shaking, on the other hand, is liable to disturb and loosen the adsorbed emulsifier, and hence more shakes are necessary, the number being correlated with the rapidity of shaking.

It might be thought from this that intermittent shaking would favor adsorption in the present case, and give a C in W type; but ordinary intermittent shaking is vigorous usually and, as one shake only is necessary to give the C in W type, must be avoided as liable to bring about partition of the gelatine. Hence in order to form the C in W type, very gentle shaking, previous partial rotation, or very gently intermittent shaking is necessary; adsorption of gelatine on the cresylic acid globules then commences and becomes firmly established with little fear of immediate partition of the emulsifier, and any further hand-shaking then gives the C in W type, the usual instability of this type being possibly due to the presence of unemulsified cresols consequent on this preparatory procedure, to the solution of the protective layer of gelatine by the cresylic acid external phase, when the gelatine was originally dissolved in the water, and by the water internal phase when originally dissolved in the cresylic acid.

---

[1] Briggs: J. Phys. Chem., 24, 120 (1920).

[2] Nugent: Trans. Faraday Soc., 17, 703 (1922).

[3] Woodman: J. Pomology and Horticultural Science, 4, 95 (1925).

The above explanation of the formation of the C in W type is manifestly feasible when the gelatine is first dissolved in water, because adsorption usually seems to take place from the external medium; in the case where the gelatine is first dissolved in the cresylic acid, and yet a C in W type can be formed, it must be assumed that the adsorbed layer comes from the internal phase itself.

The above-mentioned hypotheses are by no means rigid, yet they give some explanation of the cases of systems where the usual thermodynamic theory—that the phase which wets the emulsifier becomes the external medium—is complicated by the "solubility" of the emulsifier in both phases. Until more work is done on the partition of a large-moleculed substance such as gelatine between solvents in which colloidal aggregation may occur, and on the surface forces of the resultant solutions, little light can be thrown on the subject. The hypotheses, however, can be adopted to explain various phenomena observed:

A new solution of gelatine, with its tendency to give W in C emulsions, is definitely emulsoid, the solid network being negligible; heating an old solution, "a reversal of the ageing process" (destroying the solid structure to give a new definitely emulsoid solution), also tends to predispose to the W in C type, even when the aged solution in the cool will give the reverse type only. Now raising the temperature facilitates the formation of emulsions of oil in soap solution[1], probably by reason of an increase in the rate of adsorption (though not increase in total adsorption), whereas in the case of gelatine as emulsifier, higher temperatures make emulsification more difficult[2], possibly because of lack of solid debris, obtained on shaking, which is necessary to form the desired rigid protective film. If then, a new solution of gelatine is used, or emulsification is caused to take place at a high temperature, the lack of solid particles would be a bar to the adosprtion required to form the C in W type, and emulsification would be possible only after partition of the gelatine, a W in C type resulting.

An old solution of gelatine will, on shaking, give large particles of debris, possibly much too large to be easily dissolved by the cresylic acid, though still very suitable for adsorption purposes. Any shaking would then tend to give a C in W type, as a large proportion of these particles would probably not take place in the partition, the water phase being rich in gelatine. The same consideration applies to C in W emulsions which have completely broken, and W in C types which have partially broken; the aqueous gelatine is old, out of solution, and difficult of solution by the cresylic acid. Re-shaking, therefore, effects a new partition exclusive of this solid material, which is in excess in the water phase, and therefore a C in W emulsion results.

---

[1] Woodman: J. Pomology and Horticultural Science, 4, 95 (1925).

[2] Woodman: Unpublished data.

Summary

Both types of emulsion are possible in the systems cresylic acid (or o-, m- and p-cresols)—gelatine—water; marked excess of one liquid phase determines the type formed, this liquid becoming the external phase.

In certain cases both types of emulsion are possible when the constituents of the system are not varied in absolute amount, the type formed depending primarily on the mode of preparation, gentle shaking (usually short shakes), or previous partial rotation favouring the C in W type, and vigorous shaking (usually long shakes), the reverse type.

The W in C type is usually more stable than the C in W type—possibly due to the fact that total emulsification of the cresols rarely takes place, the excess disperse phase liquid hastening creaming and cracking.

There are indications that where the proportions of constituents in the system are such as to make the two types of emulsion possible, an absolutely new gelatine solution would give only the W in C type, medium-aged solutions both types, and old solutions the C in W type, these C in W emulsions probably being stabler than others.

In all cases tried where the proportions are such as to make both types possible, a C in W emulsion which has completely broken gave a C in W type on re-emulsification by any manner of hand-shaking; in some cases tried, it was observed that re-shaking a creamed W in C emulsion by any method caused reversal, particularly when the emulsion was old.

A tentative explanation of the above phenomena is given.

School of Agriculture,
Cambridge,
England.
Dec. 19, 1925.

THE BENZYLATION OF AMINES. PART III

BY DAVID HENRY PEACOCK

In a previous paper[1] attention was drawn to the effect of concentration upon the velocity coefficient of the reaction between amines and benzyl chloride and to the effect of the constitution of the amine upon the character of this concentration effect. In the present paper an attempt is made to indicate the manner in which these alterations in the value of the velocity constant may be produced.

The effect of concentration upon the velocity of reaction between alkyl halides and sodium alkyloxides, phenoxide or naphthoxide has been frequently observed[2]. The observations have been explained on the assumption that ionisation of the alkyloxide, etc., takes place to an extent depending on the dilution, the ions and undissociated molecules then reacting independently with the alkyl halide[3]. If this were the whole explanation the velocity constant in any particular experiment would be expected to alter during the progress of the reaction; this is frequently found not to be the case[4]. The catalytic effect of the sodium halide formed also disturbs the course of the reaction. Burke and Donnan[5] found that in the reaction between alkyl halogen compounds and silver nitrate the velocity constant apparently depended on the concentration of the nitrate group whether present as silver nitrate or alkyl nitrate. Slator and Twiss[6] found that certain alkyl bromides when reacting with sodium thiosulphate gave higher values for the velocity constant in more dilute solution.

Conant and Hussey[7] found that for the reaction between potassium iodide and alkyl chlorides alteration in concentration produced no marked effect upon the value of the velocity constant.

Menschutkin[8], was apparently the first to observe the effect of concentration upon the velocity constant of the reaction between alkyl halogen compounds and amines; for the reaction between allyl and methyl bromides and various amines the velocity constant and the concentration are connected by the relation $KV = \text{const.}$, where V is the dilution. Thus the velocity constant decreased as the dilution increased. Rheinlander[9], found that the velocity constant of the reaction between aniline and the nitrohalogen benzenes increased as the concentrations of the reactants decreased; the effect of alteration in the concentration of the halogen compound was less marked than that produced by the aniline. Monomethyl aniline showed similar effects but to a smaller extent than did aniline. Owing to the power of forming additive compounds with bases possessed by the nitro compounds of benzene[1], this case is somewhat complicated and is undergoing further examination.

---

[1] J. Chem. Soc., **127**, 2177 (1925).

[2] Cf. Hecht, Conrad and Bruckner: Z. physik. Chem., **4**, 273 (1889); Cox: J. Chem. Soc., **119**, 142 (1921); Segaller: **103**, 1154 (1913).

[3] Cf. Shroder and Acree: J. Chem. Soc., **105**, 2582 (1914).

[4] Cf. Segaller: loc. cit.

[5] J. Chem. Soc., **85**, 555 (1904).

[6] J. Chem. Soc., **95**, 99 (1909).

[7] J. Chem. Soc., **47**, 476 (1925).

[8] Z. physik. Chem., **34**, 157 (1900).

[9] J. Chem. Soc., **123**, 3110 (1923).

The present author has found that alteration of the concentration of benzyl chloride produced little effect upon the velocity constant of the reaction with amines. Changes in the concentration of the base produced effects depending on the nature of the base. Aniline and o-toluidine showed an increase in velocity constant when the concentration of the base was increased; p-toluidine, p-chloraniline, monoethylaniline showed only a slight alteration in velocity constant; dimethyl aniline, diethylaniline and dimethyl-p-toluidine showed a very marked decrease in velocity constant when the concentration was increased. The activation energy for the reaction also showed changes depending on the concentration of the reactants; within the limits of experimental error it appeared as if the value for the energy of activation approached a limiting value as the concentration of the reactants diminished.

Table I contains the results; those marked (a) are from J. Chem. Soc., **125**, 1975 (1924) and those marked (b) from J. Chem. Soc., **127**, 2177 (1925).

TABLE I

Velocity Constants for the Reaction with Benzyl Chloride
Ethyl Alcohol as Solvent. (a)

Concentration of Benzyl Chloride	Concentration of Aniline	Temperature	K × 10^5
2 M	4 M	40°	354
1 M	4 M	"	383
1 M	2 M	"	300
0.4 M	1.6 M	35°	157
0.2 M	1.6 M	"	148
0.2 M	0 8 M	"	122

In the case of reactions between alkyl halogen compounds and organic bases it does not seem possible to apply the ionic explanation as used for the sodium alkyloxides etc., by Acree (loc. cit.) and others. The formation of reactive complexes between the solvent and the reactants would only explain changes in velocity constant at comparatively high concentration and changes only in one sense; for if an amine A and the solvent S combined thus:—

$$A + S \rightleftharpoons AS$$

---

[1] Bamberger: Ber., **33**, 102 (1900); Sudborough and Picton: J. Chem. Soc., **89**, 583 (1906).

TABLE II

Velocity Constants, Aniline, etc., and Benzyl Chloride in Methyl Alcohol at 35° and 45°

Base	Conc	Concentration of Benzyl Chloride	$k_{35°} \times 10^3$	$k_{45°} \times 10^3$	E, calories
(b) Aniline	1.6	0.4	4.25	11.2	18,780
" "	1.6	0.2	4.07	10.55	18,460
" "	0.8	0.2	3.68	9.2	17,770
" "	0.4	0.2	3.62	8.5	16,550
(b) o-Toluidine	1.6	0.2	——	7.1	——
" "	0.8	"	——	5.96	——
" p-Toluidine	1.6	"	6.21	15.1	17230
" "	0.8	"	5.90	14.7	17440
" p-Chloraniline	0.8	"	——	5.08	——
" "	0.4	"	——	5.15	——
" Monoethyl aniline	1.6	"	——	1.13	——
" "	0.8	"	——	1.13	——
" Diethyl aniline	1.6	"	——	0.303	——
" "	0.8	"	——	0.400	——
" "	"	0.1	0.178	0.377	14550
(b) Dimethyl	1.6	0.2	2.23	5.06	15890
" aniline	0.8	"	2.78	6.09	15210
"	"	0.1	2.90	6.23	14430
"	0.4	"	3.13	6.99	15580
" Dimethyl	0.8	0.1	5.75	11.5	13440
" p-toluidine	0.4	"	6.58	12.9	13470

then [AS] would be proportional to the original concentration of the amine as soon as the concentration of S, the solvent, increased to such an extent that the changes in its concentration produced by the above reaction became negligible. The effect of concentration upon velocity constant is not however negligible at low concentrations and is not always in the same sense. The assumption of the formation of a complex between the two reactants as a precedent to reaction is also insufficient to explain the effects of concentration. Hawkins[1] who examined the freezing point curves for mixtures of allyl bromide and pyridine with various solvents concluded that his results afforded no evidence for the existence of solvent-solute complexes.

The hypothesis of activated molecules offers a qualitative explanation of the observed facts if it be assumed that activation of one linkage or group of atoms can occur without other parts of the molecule being affected and that the energy of activation associated with one part of a molecule can be transferred to another under suitable conditions. A molecule of aniline can be activated in several ways; the 2, 4, 6 positions in the molecules may become reactive or the two hydrogen atoms of the amino group or the nitrogen atom may be brought to a state in which it readily becomes pentavalent, forming the nucleus of a positive ion. In the reaction between benzyl chloride and aromatic bases the essential reaction is probably the conversion of the trivalent nitrogen atom into this positive ion; this does not necessarily imply ionic dissociation as the ionisation may be intramolecular. Looked at from another point of view the above statement implies that the "lone pair" of electrons in the trivalent nitrogen atom have to be activated before they become available for the formation of the new bond involved in the formation of pentavalent nitrogen. The similarity in the behaviour of primary, secondary, and tertiary amines with benzyl halogen compounds and with alkyl halogen compounds supports this view. Nuclear substitution produces similar effects upon the rate of reaction of a primary amine and of a tertiary amine with benzyl chloride e.g. p-toluidine and dimethyl p-toluidine react faster with benzyl chloride than do m-toluidine and dimethyl m-toluidine. Similar results have been observed with other halogen compounds of Menschutkin (loc. cit.) and E. R. Thomas[1]. Substitution in the nucleus of benzyl chloride produces similar effects on the rate of reaction with both dimethylaniline and aniline thus, m-nitrobenzyl chloride reacts faster than p- in both cases. The result with aniline could be explained by assuming that reaction primarily occurs with the hydrogen of the amino group but by analogy with dimethylaniline and ethyl methyl aniline it is reasonable to assume that the reaction takes place through a stage in which a pentavalent nitrogen atom is formed. A primary amine, such as aniline reacts in the normal way with benzyl chloride when the nitrogen atom is activated. The other modes of activation of the aniline molecule are not directly useful in this reaction but under ordinary conditions we may assume that all six reactive forms are present in equilibrium in a solution of aniline. When one form is removed by reaction then the equilibrium is displaced and interchange of energy between inactive forms and forms activated in other ways may take place in order to restore the balance. .

---

[1] J. Chem. Soc., **121**, 1170 (1922).

The possibility of interchange of energy of activation by collision has frequently been postulated in gaseous reactions and does not seem improbable in the case now considered[2]. If activation be assumed to be the result of the absorption of radiation then transference of energy from one active centre to another may take place through the intervention of radiation. However the interchange takes place there is also the possibility of its being governed by quantum considerations. In such a case the assumption is allowable that, as in the case of the photo-electric effect, a quantum of insufficient amount will fail to produce activation whereas energy in excess of that necessary for activation may be converted to kinetic energy. As the probability of an effective collision between an inactive molecule and an activated will depend upon concentrations of the reactant and of its activated forms the velocity constant should increase with increase in the concentration of the reactant, e.g. aniline. Aniline molecules activated in the 2, 4, or 6 nuclear positions and in the two hydrogen atoms of the amino group act as reservoirs for the supply of energy to the inactive form when the inner equilibrium between all forms is disturbed. In the case of secondary bases and p substituted primary bases one of these possible centres of activation has been removed and there is thus not the same reservoir of activated molecules to draw upon. Tertiary bases and their derivatives have still fewer centres of activation and in their case any increase in the concentration of the base will produce a still smaller effect upon the velocity constant.

---

[1] J. Chem. Soc., **103**, 595 (1913).

[2] Cf. Mitchell: Proc. Nat. Acad. Sci., Washington, **11**, 1925); Taylor and Marshall: J. Phys. Chem., 29, 1140 (1925); Franck: Naturwiss. **47**, 1063 (1924); Fowler: Proc. Camb. Phil. Soc., **22**, 793 (1925); Tolman: J. Am. Chem. Soc., **47**, 1524, 2652; Lewis and Smith: 1508 (1925); and others.

It is next necessary to deal with the effect of the active form of the solvent. If interchange of energy can take place between the activated solvent molecules and the inactivative reactant then for all except very high concentrations of the reactant the concentration of the active form of the solvent will be constant since the solvent concentration will be constant; this however will not be true if the active form of the solvent forms a complex molecule with the solute. The probability of an effective collision between inactive solute and activated solvent will depend therefore only on the concentration of the reactant as long as the temperature and the nature of the solvent are unaltered. This effect will therefore be of a lower order as regards concentration of the reactant than the effect of the other active forms of the reactant itself. From the experimental results it seems that this effect is either itself inversely proportioned to the concentration of the reactant or is linked with other factors which produce this result.

The interval of time between the collisions of the two reactants increases as the concentration of each reactant decreases and thus the possibility of activation by collision with activated solvent before collision with the other reactant increases; so also does the possibility of collision of an activated reactant molecule with an inactive solvent molecule. But the concentration of activated solvent molecules cannot rise above the equilibrium value for the conditions concerned, there is no loss of activated solvent molecules by reaction as there is of reactant molecules. The exchange of energy between solute and solvent is therefore practically unilateral and as the time interval between collisions of the two reactants increases i.e. as the concentration decreases, the opportunity for activation by collision with active solute molecules increases and so the velocity constant increases. This effect is observed with benzyl chloride and tertiary aromatic bases.

The effect of concentration upon the velocity constants for the reaction between benzyl chloride and the aromatic bases examined follows the following order:—primary bases (not *p*-substituted) $k = f(c^{a})$, secondary bases and *p*-substituted primary bases $k = f(c^{\circ})$, tertiary bases $k = f(c^{-b})$. The order deduced with the help of the considerations indicated above is:—primary non *p* substituted bases $k = f(c^{p+q+1})$, secondary bases and *p* substituted primary bases $k = f(c^{q+1})$, tertiary bases $k = f(c)$. If the effect of the solvent is also considered, then, as indicated above, for tertiary bases $k = f(c^{-1})$ whence the other equations become $k = f(c^{q-1})$ and $k = f(c^{p+q-1})$, the same order as found experimentally.

The activation of the molecules of the reactants by collision with activated solvent molecules has obviously a close bearing upon the effect of the solvent upon the rate of reaction. The rate of reaction will tend to be greater in those solvents which possess the greatest concentrations of activated molecules i.e. which are themselves most reactive. The results obtained by Menschutkin[1], Table III, support this to some extent.

TABLE III

Velocity of Reaction between Ethyl Iodide and Triethylamine, Menschutkin (loc. cit.)

Solvent	k, (comparative)	Solvent	k, (comparative)
Hexane	1	Phenetole	117.7
Heptane	1.3	Ethyl Alcohol	203.3
Benzol	38.2	Benzyl Alcohol	742.2
Chlorbenzol	128	Acetone	337
Brombenzol	150	Acetophenone	718
Diethyl ether	4.2		

Hawkin's results for the reaction between alkyl bromide and pyridine at 28.3° are as follows:—

> toluene 0.00023, benzene 0.000305, nitrobenzene 0.0129, *p*-nitrotoluene 0.00657 acetone 0.00505, acetophenone 0.0104 alcohol 0.00251.

Benzene hydrocarbons are more reactive than aliphatic and reactions in them show a higher velocity constant. Their derivatives show similar behaviour, cf. acetone and acetophenone, ether and phenetole, ethyl alcohol and benzyl alcohol.

The probability of interchanges of energy between the activated molecules of solvent and the unactivated molecules of the reactants may not be independent of the nature of the reactants and hence the solvent which has the greatest reactivity will not necessarily be the solvent in which the reaction measured takes place with the maximum velocity. In this connection it is also necessary to repeat that the reactivity of the solvent as ordinarily measured is a property dependent on the behaviour of the solvent towards some other reactant and will vary with the reactant chosen. It is possible that if the energy of activation of the solvent were less than that of the dissolved reactants no activation of the latter could take place.

If, in a given solvent, two or more reactions take place simultaneously, requiring for their fulfilment two or more kinds of activated molecules then the solvent will favour that reaction for which the interchange of energy between activated solvent molecules and unactivated reactant molecules takes place with the most ease. This reaction will not necessarily be that which require the least energy of activation as the ease of activation will be governed also by steric effects[1].

---

[1] Z. phys. Chem., **6**, 41 (1890).

The solvent may also alter the velocity of a reaction by altering the energy of activation of the reacting molecules. The measured energy of activation in the case of dimethylaniline and benzyl chloride seems to approach a minimum but these results must be accepted with caution as to the energy of activation is not a quantity susceptible of measurement with great accuracy and it is difficult to decide whether the change in the measured energies of activation is real or due to experimental error. If activation is a process affecting a molecular species which is also in equilibrium with other species then the energy of activation measured will include the thermal effects of the other equilibria involved. Whatever the final causes an alteration in energy of activation due to change in concentration will be reflected in the values of the velocity constants concerned. Thus in the case of dimethyl aniline and benzyl chloride part of the effect of concentration upon velocity constant can be attributed to its effect on the energy of activation.

Further work is in progress on this subject with derivatives of benzyl chloride and with halogen derivatives of nitro-benzene.

University College,
Rangoon, Burma.
February 24, 1926.

---

[1] Cf. Bjerrum: Z. physik. Chem., **108**, 85 (1924); Brönsted: **102**, 169 (1922).

VELOCITY OF THERMAL DECOMPOSITION OF CARBONATES*

BY B. BRUŽS[1]

The problem of the thermal decomposition of carbonates has been undertaken with two objects in view. Firstly to bring some light on the question why many of the heterogeneous equilibria between solid substances and gases can be attained only by way of decomposition, the equilibrium pressures not being regained when the reaction is reversed. Secondly the kinetics themselves promised to give interesting results regarding the influence of temperature on reaction velocities, as previous experience with some carbonates showed that the process of decomposition could often be interpreted by means of the usual homogeneous reaction equations.

The classical theory of a dynamic equilibrium for solid-gaseous systems in general and carbonates-carbon dioxide and salt-hydrates-water vapor in particular is mainly due to the early work of C. L. Berthollet[2], H. Rose[3], H. Sainte-Claire Deville, Debray[4], and Pfaundler[5].

The general conclusion of this work can be summarized as follows. At equilibrium, the velocities of decomposition and recombination are equal and, therefore, the pressure of the gaseous phase is determined by the temperature. Ample experimental proof was accumulated by the same authors to show the catalytic activity of water in the case of the thermal decomposition of carbonates.

The question has obtained its thermodynamic solution in the "exact" formula of Nernst for calculation of equilibrium constants of chemical reactions and, in a special case, the "approximation formula" of Nernst for the equilibrium constant for a carbonate

$$\log p = -Q/4.571T + 1.75 \log T + 3.2$$

enables one to determine approximate carbon dioxide pressures for any carbonate from the knowledge of the heat of the reaction

$$MeO + CO_2 = MeCO_3 + Q.$$

But, some very large discrepancies in the experimental determinations of carbon dioxide pressures and theoretical considerations (Langmuir) have cast doubts on the validity of the kinetic explanation of the equilibrium. Nernst has introduced in his work the idea of the equilibrium taking place in the gaseous phase, where all components are supposed to be present in the form of their saturated vapor. Ostwald has called attention to the improbability of such an assumption. It is difficult to imagine substances like calcium oxide having appreciable vapor pressure.

---

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Charlotte Elizabeth Procter Fellow.

[2] Essaide Statique chimique, 48-53 (1803).

[3] Pogg. Ann., **82**, 545 (1851); **55**, 415 (1842).

[4] Compt. rend., **64**, 603 (1867); **79**, 890 (1874).

[5] Pogg. Ann., **131**, 55 (1867); Jubelband 182 (1874).

Another explanation which would replace the mechanisms of Berthollet and Nernst was given by Langmuir[1], who proposed the idea of a reaction taking place at an interface metal oxide-metal carbonate or salt hydrate-salt respectively.

No extensive investigations have been made of the velocities in question. The first case was studied by G. N. Lewis[2], who investigated the decomposition of silver oxide and found the reaction to obey the equation of an autocatalytic reaction, where silver plays the rôle of the catalyst. But, his final conclusion was that he really measured the velocity of the reaction $2O = O_2$ in presence of silver. Hinshelwood and Bowen[3] and Hinshelwood[4] investigated a number of substances, most of them of an explosive character and are inclined to believe in interface reactions. Some analogous results in cases of mostly autoaccelerated reactions have been obtained by Sieverts and Theberath[5], Otto and Fry[6], and Crowther and Coutts[7]. Reaction velocities not showing acceleration have been described by Centnerszwer and Bružs[8].

The Apparatus

The main aim of the apparatus employed is to investigate the reaction from its very beginning and secondly to conduct it at constant temperature and pressure. Fig. 1 gives a schematic idea of the apparatus.

The substance is placed in the reaction vessel A, a narrow glass tube and connected through the ground seal B to the gasholder C, an iron vessel of large size. On account of the largeness of the vessel the gas remains practically at the original pressure when not more than 100 ccm. of gas are collected in it. The gasholder is kept at constant temperature (25°) in a thermostat K. This arrangement permits an investigation of the reaction at different pressures, although most of the experiments in this investigation have been conducted at atmospheric pressure. Through the stopcock F the apparatus is filled with carbon dioxide. When the reaction takes place, the gas pressing on the surface of the mercury in C causes mercury to flow over in D. The overflowing mercury is collected in E and gives a measure of carbon dioxide evolved in the reaction. G is an iron block, the furnace, heated by nichrome wire wound around it. It has two drilled holes, just fitting the reaction vessel and the thermometer I. Besides that there is a larger hole (not shown in Fig. 1) for a larger reaction vessel. The furnace is very carefully insulated with asbestos and magnesia, so that for temperatures up to 700° it does not require more than 1.5 amps. (at 110 volts) and makes hand regulation with an ammeter and resistance very easy. The temperature in the experiments very seldom fluctuated more than ± 0.1°.

---

[1] J. Am. Chem. Soc., **38**, 222 (1916).

[2] Z. physik. Chem., **52**, 310 (1905).

[3] Phil. Mag., (6), **40**, 569 (1920); Proc. Roy. Soc., **99A**, 203 (1921).

[4] J. Chem. Soc., **119**, I, 721 (1921).

[5] Z. physik. Chem., **100**, 463 (1922).

[6] J. Am. Chem. Soc., **45**, 1134 (1923).

[7] Proc. Roy. Soc., **106A**, 215 (1924).

[8] Acta Univ. Latviensis **11**, (1924); Z. physik. Chem., **115**, 365 (1925); J. Phys. Chem., **29**, 733 (1925).

The Velocity of Decomposition of Ferrous Carbonate

From the number of carbonates investigated in this research with respect to their velocities of thermal decomposition the crystalline natural siderite can be described first on account of the simplicity of this process. The velocity of decomposition of very pure large crystals of siderite of about 0.4 gr. has been measured in the range of 491°-581°C. The decrease of the velocity of carbon dioxide evolution with time clearly showed that the process can be described by the formula of a unimolecular reaction.

For the sake of simplicity and convenience the following method of calculation has been applied. The volume of carbon dioxide evolved during fixed intervals of time (1/2 min.-20 min., depending on the temperature of the experiment) was accepted as a measure of the velocity of decomposition in the interval. The velocity of a unimolecular reaction decreases with time according to the formula:

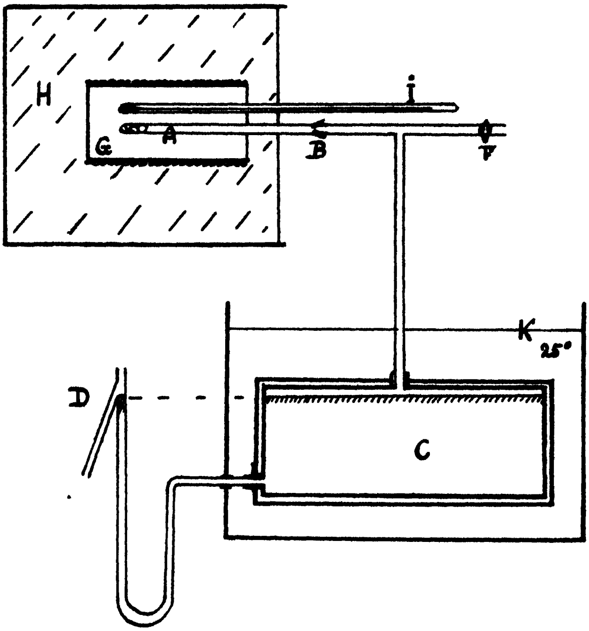


Fig. 1

$$I_t = I_0 e^{-\lambda t}$$

where I_t is the velocity at the moment t, I_0 the initial velocity and λ the reaction constant.

From this equation the following relation is easily derived

$$\lambda = \frac{\ln I_{t_1} - \ln I_{t_2}}{t_2 - t_1}$$

in words: the slope of the straight line representing the plot of the logarithms of the velocities against time gives the constant of the reaction.

In fact the data of all experiments except the one experiment at the lowest temperature (491°) when plotted in the way mentioned above gave straight lines. The constants[1] of the reaction for the different temperatures obtained by this calculation are given in Table I.

TABLE I

C°	λ	λ calc.
491	.00805	
501	.0106	.011
511	.0221	.022
521	.0442	.044
531	.0851	.085
540	.154	.150
541	.191	.180
550	.352	.290
553	.301	.350
561	.607	580
566	.667	.780
573	.989	1.18
581	1.472	1.90

When the logarithms of the reaction constants were plotted against the reciprocals of the absolute temperature a straight line resulted, which meant that the Arrhenius formula for the relation between reaction constants and temperature was valid for this reaction. The value of the critical increment E of the Arrhenius formula

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_{T_2}}$$

has been calculated from the reaction constants at 501° and 561°. E was found to be 85,500 cals. How closely the observed values agree with the values recalculated from the Arrhenius equation is shown by the third column of the table. Table II shows the calculated percentage decomposition compared with the observed values for eight experiments in a wide range of temperature.

A marked deviation can be seen in the two latter experiments, but one must take into consideration that a deviation of 15 percent is not too high for a reaction the half-lifetime of which is 0.58 min.

Two further questions were investigated in connection with the decomposition of siderite.

As has been noted above, the experiment for the lowest temperature gave an abnormal value for the velocity constant. To settle this question 5 experiments were conducted at low temperatures with large siderite crystals (3-4 grams). In all cases the velocities had very low values and the plots of

---

[1] All constants are calculated with the use of natural logarithms and are given in reciprocal minutes. Time is given in minutes.

TABLE II

	501°	
time	% decomposed	
	calc.	obs.
20	20	22
40	36	38
60	48	50
80	59	59
100	67	67
120	73	73
140	79	79
160	83	83
180	86	

	511°	
time	% decomposed	
	calc.	obs.
10	20	22
20	36	38
30	48	49
40	59	59
50	67	67
60	73	73
70	79	78
80	83	82
90	86	86
100	89	

	521°	
time	% decomposed	
	calc.	obs.
5	20	20
10	36	36
15	48	48
20	59	58
25	68	66
30	74	72
35	79	
40	84	82
45	87	86
50	90	90

	531°	
time	% decomposed	
	calc.	obs.
2	16	16
4	29	29
6	40	40
8	49	50
10	57	58
12	64	64
14	70	70
16	74	75
18	78	79
20	82	82
22	85	
24	87	
26	89	88

	541°	
time	% decomposed	
	calc.	obs.
1	16	16
2	30	30
3	42	42
4	51	51
5	59	59
6	66	66
7	72	71
8	76	76
9	80	79
10	84	82
15	93	91
20	97	94

	553°	
time	% decomposed	
	calc.	obs.
1	30	28
2	50	49
3	65	63
4	75	74
5	83	81
6	88	87
7	91	91
8	94	94
9	96	
10	97	97
11	98	98
12	99	99

	561°	
time	% decomposed	
	calc.	obs.
0	44	33
1	69	57
2	82	75
3	90	86
4	95	93
5	97	96
6	98	98
7	99	99

	573°	
time	% decomposed	
	calc.	obs.
0.5	45	36
1.0	69	63
1.5	83	79
2.0	91	86
2.5	95	92
3.0	97	95
3.5	98	
4.0	99	99

the logarithms of the velocities against time showed indeed a linear course; but, one could readily see that the velocity of carbon dioxide evolution would reach zero before the substance would be totally decomposed. Still, the slope of the curve was calculated as by this process we eliminate the time factor. The percentage decomposition which could be achieved if the reaction were continued until the velocity had reached zero can then be readily extrapolated from the slope of the curve and the initial velocity I_o as

$$I_o = \lambda N \text{ and } N = I_o/\lambda$$

If we give the value of N so obtained a meaning of "active mass" then λ becomes the reaction constant. Table III gives these values.

TABLE III

C°	λ	N
445	.0035	
455	.0064	9 percent
465	.0058	14 "
485	.0058	50 "
495	.0074	100 "

We must draw from these experiments the conclusion that in the range of temperature between 455°-495° the velocity constant of the reaction remains practically constant and only the active mass increases with temperature. Above 495° the active mass reaches the value of 100 percent.

It is worth while noting at this place that the samples of the siderite after this partial decomposition were investigated with respect to interface formation, but, it was found that even the largest and least decomposed samples had turned black uniformly throughout the whole crystal.

The second question investigated concerned the dependence of the reaction constant upon the state of grinding. Crystals from the same batch of siderite that had been used in the previous experiments were ground and sieved through screens; a uniform fraction of powder was collected between two screens of close mesh number and used for five experiments. The average size of the crystals measured under the microscope was 0.3 mm. The curves representing the plot of the logarithms of the velocity against time again showed a straight line relationship and the reaction constants could be easily calculated. They are given in Table IV.

TABLE IV

C°	λ	
485	.0065	N = 60 percent
495	.0065	
505	.0166	
515	.0414	
525	.0966	

Here again we see the same fact that the reaction constant for temperatures below 495° is too high, namely at 485° it is as high as the reaction constant at 495° but, as in the previous case, the reaction does not tend to go to completion. The "active mass" is only 60 percent.

The constants for the four experiments carried out at temperatures at and higher than 495° lie on a straight line, when their logarithms are plotted against the reciprocal absolute temperature. The critical increment is higher than in the reaction with a single crystal, it is 110,800 cals..

It must be mentioned that the velocity of a small part of the initial stage of the reaction exceeds the values to be expected from the greater part of the reaction. This small deviation seems to be due to small amounts of very fine dust of broken crystals. This observation is in accord with the higher value for the critical increment found with the smaller crystals.

Velocity of Decomposition of Synthetic Ferrous Carbonate

Synthetic ferrous carbonate has been prepared by the method of Sénarmont, by the action of a concentrated ferrous chloride solution on calcium carbonate at 170°. The carbonate obtained, when dried, lost, together with the water, about 20 percent of its carbon dioxide. It readily dissolved in cold acids.

Nevertheless, some experiments carried out with this preparation which did not yield any definite results, still gave an idea about the velocity of decomposition, and mainly the important fact that decomposition at 760 mm. carbon dioxide was complete at 340° as compared with a temperature of 495° for the naturally occurring mineral.

Below 340° the decomposition is not complete and the reaction velocity is of the order of .004-.006 min.$^{-1}$. Three experiments above 340 gave better results. The constants obtained were

340°	.0110
350°	.0152
360°	.0239

and their logarithms when plotted against the reciprocal absolute temperature gave a straight line, which permitted one to calculate the critical increment 30,700.

The Velocity of Decomposition of Cobaltous Carbonate

Cobaltous carbonate has been prepared in a dry and crystalline state by the action of a saturated cobaltous chloride solution during twenty-four hours on calcium carbonate powder in a sealed tube at 170°C. This method of synthesis, described by Sénarmont[1] has been applied because simple drying of the common carbonate in a stream of carbon dioxide does not yield the anhydrous carbonate. The crystalline anhydrous cobaltous carbonate is reminiscent of some natural carbonates by reason of its very slow solubility in acids.

The results of a series of 5 experiments made at temperatures ranging from 427°C. to 477°C. were plotted in the following way. The scale of the abscisse (time) has been increased by 100 percent for every succeeding experiment, which is always made at 10° higher than the preceding one. The ordinate represents the percentage of cobaltous carbonate decomposed. Under these conditions the initial course of the curve falls together for all experiments. The further run of the curve shows marked divergencies. In other words, the temperature coefficient for the initial stage of the reaction is very close to 2 for a 10° rise and is higher than two in the final stage.

---

[1] Ann. Chim. Phys., (3) **30**, 138 (1850).

The course of the individual curves has been analysed by plotting the logarithms of the reaction velocity against time and it has been found that the curve obtained is a straight line for the initial stage of the reaction, changes quite abruptly its slope at a certain point and continues then again as a line up to the end of the reaction. The same characteristic behaviour is shown by the plot of the reaction velocity against the percentage of decomposition.

This observation and previous experience with analogous curves lead to the conclusion that the decomposition takes place in two stages and most probably according to the scheme:

$$CoCO_3 \longrightarrow CoCO_3 . CoO + CO_2$$
$$CoCO_3 . CoO \longrightarrow CoO + CO_2.$$

This theory would further account for the fact that the temperature coefficient as mentioned above is about 2 in the first stage and higher for the second half of the reaction, the cause being that the first stage represents the first and fast reaction, the rest of the curve the second and slow reaction. The second reaction begins at higher temperature and would naturally be expected to have a higher temperature coefficient as the temperature coefficient, with other conditions maintained the same, decreases with increase of temperature.

To test the assumption, the experimental data have been compared with values theoretically to be expected. The constant of the first reaction has been evaluated from the initial velocity of the reaction, where the second reaction does not yet play an appreciable rôle. This can be done by the use of the formula

$$I = N\lambda_1 \qquad \text{and} \qquad \lambda_1 = I/N,$$

where I is the velocity of the reaction in percent per minute, λ_1 the reaction constant and N the active mass, here according to our assumption 50 percent (carbon dioxide). The constant of the final reaction has been evaluated from the final slope of the curve representing the plot of the logarithms of the velocities against time, here

$$\lambda_2 = \frac{\ln I_1 - \ln I_2}{t_2 - t_1}$$

where t is the respective time. Both constants then have been substituted in the theoretical equation for the assumed reactions:

$$CO_2 = \frac{a}{2}\left(2 + \frac{2\lambda_2 - \lambda_1}{\lambda_1 - \lambda_2}e^{-\lambda_1 t} - \frac{\lambda_1}{\lambda_1 - \lambda_2}e^{-\lambda_2 t}\right)$$

where CO_2 means the percentage of the total amount of carbon dioxide (a) evolved at the time t from the beginning of the reaction and λ_1 and λ_2 are the reaction constants of the first and second reactions respectively. The agreement between observed and calculated values can be seen from Table V.

TABLE V

447°

$\lambda_1 = .018$ $\lambda_2 = .0023$

time	% decomposed obs.	 calc.
50	34	32
100	47.8	48
150	57.5	57
200	64.0	63
250	68.0	68
300	71.6	72
350	74.2	75
400	76.0	78

457°

$\lambda_1 = .040$ $\lambda_2 = .0055$

time	% decomposed obs.	 calc.
20	28.7	28
40	42.0	44
60	51.2	54
80	58.5	61
100	63.8	65
120	68.3	70
140	72.3	72
160	75.5	75

467°

$\lambda_1 = .0805$ $\lambda_2 = .0115$

time	% decomposed obs.	 calc.
10	29.6	29
20	44.0	41
30	54.7	55
40	62.8	62
50	68.6	66
60	73.8	70
70	77.5	74
80	80.6	76
90	83.1	80
100	85.1	82
110	86.7	84
120	88.2	85
150	91.0	90
360	99.5	99

477°

$\lambda_1 = .138$ $\lambda = .023$

time	% decomposed obs.	 calc.
10	41.8	42
20	62.1	60
30	73.9	69
40	81.3	76
50	85.1	81
60	88.0	85
70	90.1	88
80	91.6	90
90	92.9	92
100	94.0	94
110	94.8	95
120	95.5	96
130	96.1	97
140	96.5	98
150	96.9	98

These values permit one to calculate the critical increment of the reactions, as, in the observed range of temperature, the constants of both reactions show a linear relation between the logarithms of the reaction constants and the reciprocal of the absolute temperature. From

$$E = \frac{R}{T_2^{-1} - T_1^{-1}} \cdot \ln \frac{\lambda_{T_1}}{\lambda_{T_2}}$$

we find, substituting the values determined above the critical increments E_1 and E_2 for the first and second reactions

$$E_1 = 72{,}400$$
$$E_2 = 82{,}200$$

The Velocity of Decomposition of Zincspar

A series of thirteen experiments was conducted in the range of 407°-452°C. The substance used for these experiments was very pure natural "amorphous" zincspar; the carbon dioxide evolved in the experiments was always in close agreement with theoretical values for total decomposition.

The velocity of decomposition showed a peculair behaviour: about 65 percent of the substance was decomposed at a practically constant rate; after that, the reaction markedly slowed down and abruptly finished near the end.

No mathematical expression could be found to describe this reaction neither by postulating intermediate reaction, nor assuming a heterogeneous catalysis by zinc oxide.

The only way to find the influence of temperature was to compare the constant velocities of the main part of the reaction referred in each case to 1 gr. of carbonate. The amount of substance used in the experiments was 0.5-0.8 gr. in each run. The combined data are given in Table VI. Column 3 gives the percentage decomposition up to which the reaction velocity is constant.

TABLE VI

°C	Const.	Validity
407	.22 cm/min	38 percent
417	.49	71
423	1.94	58
427	2.54	72
427	2.35	67
430	2.60	83
432	2.23	65
437	3.84	66
437	7.13	74
438	3.32	68
442	6.66	60
447	14.65	79
452	11.50	61

The data do not give a good agreement and the deviations of the determined values from a continuous increase of this value with temperature exceed the experimental error.

A straight line drawn through the logarithms of the velocities plotted against the reciprocal of the absolute temperature gave a value of the critical increment 95,000.

When the reaction was finished the lumps of zinc carbonate were not broken and were yellow when hot and white when cool.

The Velocity of Decomposition of Cerussite

The thermal decomposition of lead carbonate represents the most complicated example of the reactions investigated here. This fact could be expected from carbon dioxide pressure measurements of lead carbonate described by Centnerszwer, Falk, and Awerbuch[1], which lead the authors to conclude that three intermediate compounds 3 . PbO . $5PbCO_3$; PbO . $PbCO_3$; 2PbO. $PbCO_3$ are formed in the course of the decomposition.

A large number of experiments was conducted with two different samples of crystalline natural lead carbonate. The results checked satisfactorily for experiments conducted in the range from 320°-350°C. with beautifully developed single crystals of cerussite weighing from 0.6-0.9 grams each. In all cases 50 percent of the total amount of carbon dioxide were evolved, which fact proves the formation of the intermediate compound PbO . $PbCO_3$, described by M. Centnerszwer, Falk and Awerbuch as stable in this range of temperature. The mathematical analysis of the decomposition curves showed that the reaction obeyed the scheme of a unimolecular reaction.

TABLE VII

°C	λ
320	0.0046
325	.0069
330	.0110
335	.0173
340.3	.0308
345.3	.0478
350	.1007

The logarithms of the reaction constants plotted against the reciprocal absolute temperature lay on a straight line. The critical increment calculated from the slope was 69,600.

The reaction curve did not indicate the formation of the intermediate compound 3·PbO . $5PbCO_3$ mentioned above. To find an explanation for this fact some experiments were conducted with larger amounts of substance (6-8 gr.) at low temperatures. The result was analogous to the one in the case of ferrous carbonate. Below a certain temperature, in this case, below 308°C. the substance does not decompose totally to form $PbCO_3$. PbO but seems to form a solid phase of variable composition with an "active mass" (N) increasing with temperature. The results are given in Table VIII.

TABLE VIII

Temp.		
296°C.	.00173	9 percent
306	.00155	49
316	.00478	50
326	.00780	50

---

[1] Acta. Univ. Latviensis 11, 289 (1924).

The product of the first stage of decomposition of lead carbonate $PbO.PbCO_3$ is a white substance. This last compound was decomposed into a reddish-brown oxide, PbO, at considerably higher temperatures. The decomposition was analogous to the case of zinc carbonate, namely, the velocity for about 70 percent of the reaction was constant and then slowed down very appreciably. This stage of the reaction was not investigated carefully enough but Table IX will give an idea of the influence of temperature on this reaction.

TABLE IX

Temp. °C.	Velocity $cm^3/gr.$ min
426	.49
436	1.32-1.64
446	2.12-2.50
456	3.50-6.15

Another substance investigated by this method was synthetic mercurous carbonate, obtained by precipitation of mercurous nitrate with potassium bicarbonate. The tendency of mercurous nitrate to hydrolyse and form a basic nitrate requires a long period of preparation, during which period the initially white substance turns slightly yellow. The product is not sufficiently pure to yield good results and therefore they will only be described briefly. The description is not omitted because this reaction differs from the previously described by its autocatalytic character.

The velocity of the reaction, very slow in the beginning once started rapidly increases to a maximum and then slows down resembling very much the curves obtained by Lewis[1] for silver oxide. The curve does not yield easily to mathematical analysis. The Ostwald formula could be best tested applying it in this

$$dx/dt = (K_1 + K_2x)(a - x)$$

differential form by plotting $dx/dt : (a - x)$ against x. The plot represented a straight line up to high values of x (a being Hg_2CO_3 and x being Hg_2O or what amounts to the same $- CO_2$). Thus values for K_1 (point where the straight line crosses the axis of ordinates) and K_2, the slope of the line could be calculated. It was found that K_1 is very small[2]. K_2 is large and represents the catalytic effect of mercurous oxide. Unfortunately this substance is unstable, which is evident from the final inclination of the straight line towards the abscissa. Thus, a complication arises on account of the gradual disappearance of the catalyst, ($Hg_2O = HgO + Hg$). The proof of this explanation was obtained by the fact that samples of the remaining oxide showed a largely decreased amount of monovalent mercury and an appearance of metallic mercury in all the cases where the curve had suffered an appreciable inclination towards the abscissa. Another evidence for the autocatalytic character of the reaction is given by the observation that mercurous carbonate blackened for an hour in sunshine without a measureable loss of carbon dioxide, decomposed much faster than the pure substance, but the catalytic power of traces of mercurous oxide seems to be confined only to its presence in closest contact, because mixtures of thermally decomposed mercurous carbonate with undecomposed material showed hardly any difference from the pure samples.

---

[1] loc. cit.

[2] Lewis in his paper on silver oxide as a matter of fact does not consider it at all, although it could easily explain the asymmetry of his curves.

Discussion of the Results

The first object of this investigation namely the factors influencing the determination of reaction pressures of carbonates has been solved insofar that it has been shown that the reaction velocities drop logarithmically towards the equilibrium point. The equilibria seem to be obtainable with any thermodynamic degree of accuracy only by increasing the sensitivity of the method so far that they can be attained from both sides. On the other hand the results can be interpreted thermodynamically only when the reactions are known. The cases of lead and cobalt carbonates show definitely that the processes are of a complex nature which must be ascertained before any pressure measurements are made.

There remains to be given a short discussion of the results of the kinetics themselves. The simplest case seems to be zinc carbonate leading to the result that a simple isothermal process of decomposition of a substance having a constant pressure p_s against an outside pressure p is proportional to the pressure difference $(p_s - p)$. As this difference under experimental conditions was constant the reaction velocity was constant also. In the case of ferrous carbonate the pressure of the carbon dioxide changes during the process with change of concentration of carbon dioxide in the solid solution. The reaction constant will be proportional to the constantly diminishing pressure difference and will yield a unimolecular reaction curve in all cases where the reaction is conducted above the temperature where the lowest pressure is one atmosphere. Below this temperature the reaction will have a unimolecular form also, but will go only to a point where the solution pressure will have fallen to one atmosphere. This gives to the value of the difference between unity and "active mass" the meaning of solubility of carbon dioxide at one atmosphere at different temperatures in the solid phase. The solubility increases with decreasing temperature. Lead carbonate undergoes both typical processes described on account of the formation of the intermediate product $PbO \cdot PbCO_3$. In the first stage carbon dioxide is soluble in this intermediate product and yields unimolecular reaction curves; in the second stage $PbO \cdot PbCO_3$ decomposes like zinc carbonate directly into PbO and carbon dioxide. Cobalt carbonate is analogous to the lead salt with the difference that both stages of the reaction are so close together that they can be differentiated only by a kinetic investigation.

The "critical increments", determined from the dependence of the reaction constants on temperature, approximate the value of 80,000 cal. and seem therefore to be characteristic of the carbonate ion in the crystal lattice[1]. In the case of synthetic ferrous carbonate the value is very much lower probably on account of the catalytic action of water. Catalysed reactions are known to have low temperature coefficients.

I wish to thank Professor G. A. Hulett and Professor H. S. Taylor for the inspiring support and interest in this investigation.

Summary

1. A method is described of investigating reactions of decomposition of solids yielding gaseous reaction products.

2. Ferrous, lead, cobalt, zinc and mercurous carbonates have been investigated by this method with the result that these substances decompose at rates in accord with those found valid for homogeneous unimolecular reactions.

3. The mechanisms of decomposition have been derived for all the substances mentioned.

4. All these reactions have high temperature coefficients the mean value for the "critical increment" 80,000 cal., seems to be characteristic of the carbonate ion in the crystal.

Princeton,
New Jersey.

---

[1] An interesting coincidence may be mentioned here. According to Schaefer and Schubert (Ann. Physik., (4) **50**, 283 (1916)) the carbonate ion in fifteen carbonates investigated by them has three characteristic bands in the infrared with maxima at 6.5, 11.5 and 14.5μ. If we calculate the "activation energy" corresponding to the three bands with the aid of the radiation theory assumption Nhv = E we get in the sum 89.000 cal., a value which is not too far from the observed one.

CRYOSCOPIC MEASUREMENTS WITH NITROBENZENE

Part IV. Association in nitrobenzene solution

BY FREDERICK STANLEY BROWN AND CHARLES R. BURY

The cryoscopic method has been largely used in the study of association in solution: it is doubtful, however, if the results of any previous investigators are sufficiently accurate to decide whether the law of mass action is obeyed. Few have paid sufficient attention to the tendency of solvents to pick up water, and the consequent error in the molecular weights: even with benzene the error due to this cause is larger than can be permitted in work having this object in view[1]; with more hygroscopic solvents, such as nitrobenzene, the error may be much greater. Previous investigators have almost invariably used the van't Hoff equation, which is known to be accurate only at low concentrations, while the law of mass action can only be tested adequately by measurements over a fairly wide range, extending to concentrations at which use of this formula is quite unjustifiable.

As the result of experience gained in previous researches on the use of nitrobenzene as a solvent for cryoscopy, we believe it possible to obtain the necessary accuracy. Roberts and Bury[2] showed that the water content of the solvent could be kept constant at any desired degree of saturation by keeping the solvent in contact with phosphorus pentoxide, water, or a salt hydrate pair. Brown and Bury[3] investigated the alleged change of cryoscopic constant with water content of the solvent. The results obtained led them to put forward an equation that was obeyed by normal substances with considerable accuracy up to concentrations that gave a depression of 4°C. Lastly, Brown,[4] by investigation of the dissociation of naphthalene picrate and naphthalene-trinitrotoluene, equilibria which are known from independent work to obey the law of mass action, was able to show that these methods are sufficiently accurate for the purpose in view.

The method used to keep the water content of the solvent constant lends itself admirably to the study of the influence of the degree of moisture of the solvent on the association of solutes. In view of the interesting results obtained by Baker with pure liquids we have extended our work to the investigation of this problem.

Experimental

The usual Beckmann method was employed: the preparation of pure nitrobenzene and the use of salt hydrate pairs for keeping the water content of the solvent constant have been described by Roberts and Bury (loc. cit.).

---

[1] Sidgwick: J. Chem. Soc., **117**, 1340 (1920).

[2] J. Chem. Soc., **123**, 2037 (1923).

[3] J. Chem. Soc., **125**, 2219 (1924).

[4] J. Chem. Soc., **127**, 345 (1925).

In this work nitrobenzene of three different degrees of moisture has been employed; i. e., dry, fully saturated, and partially saturated in the presence of $Na_2SO_4,0-10H_2O$.

In our choice of solutes we avoided, as far as possible, substances such as ethyl alcohol, phenol, and acetic acid, which are difficult to prepare and keep free from water: we tried, without much success, to find suitable solids, rather than liquids, for reasons of practical convenience. It is desirable that solutes should be easily purified, readily soluble in nitrobenzene at its freezing point, but should not, for reasons given below, be easily soluble in water. It is difficult to find acids that fulfil these criteria. The solutes used—benzyl and iso-amyl alcohols, β-naphthol, phenyl-acetic, propionic, cinnamic and benzoic acids—were carefully purified by crystallisation or distillation. Liquid solutes were weighed out in small glass bulbs which were dropped into the solvent and broken under its surface.

Difficulties met when working with the dry solvent, in the presence of phosphorus pentoxide, have been discussed fully elsewhere:[1] all powerful dehydrating agents (except sulphuric acid which is soluble in nitro-benzene) seem to adsorb solutes containing an hydroxyl group, and in some cases are even peptised by them.[2] In our experiments with the dry solvent, therefore, no dehydrating agent was employed; the nitrobenzene was distilled in vacuo from phosphorus pentoxide directly into the freezing point tube immediately before the experiment. The apparatus was filled with dry air, a current of which was passed through it in the usual manner throughout the duration of the experiment. Work was carried out as rapidly as possible, no series of experiments lasting more than three hours. As a rule two additions of solute were made in each series, results being checked by another series in which the highest concentration reached in the first series, after two additions of solute, was reached at once in the second series, and so on. This procedure would have enabled us to detect errors due to the absorption of moisture, but these were not observed.

A possible source of error when working with the fully saturated solvent in the presence of water, is the partition of the solute between nitrobenzene and water. If the solute is readily soluble in water, appreciable quantities may be removed from the nitrobenzene solution and the measured degree of association will be too great: also the activity of the water may be altered appreciably and the assumption that the activity of the water remains constant will be invalid. To avoid this error as much as possible, we used minimal quantities of water, and chose solutes which are not readily soluble in water. With the object of detecting passage of the solvent into the water layer, we carried out a number of experiments in which the quantity of water was varied.

---

[1] Brown and Bury: J. Phys. Chem., **29**, 1312 (1925).

[2] Alumina is an excellent dehydrating agent and adsorbs the two alcohols that we have used as solutes to a very slight extent, if at all: it has therefore been used as dehydrating agent in several series of determinations of the association of these alcohols in dry nitrobenzene. We have come to the conclusion, however, that results obtained by the method described in the text, without employing any dehydrating agent, are more reliable, and these alone are quoted.

the amounts of nitrobenzene and solute remaining constant. The error due to this cause is quite negligible except in the case of propionic acid; the results obtained with this acid in the fully saturated solvent are probably subject to a small but appreciable error due to this cause.

All freezing points recorded are the mean of at least three closely agreeing determinations, and are, we believe, usually accurate to about 0.003°C. At least two independent series were carried out with each substance. The results obtained are given in Tables I-VII. In the first column are given the concentration (C) in grams per 100 grams solvent; in the second the observed depression (D); in the third the molecular weight (M) calculated by the formula of Brown and Bury;[1] and in the fourth the degree of association (x = M/ formula weight).

Benzoic and cinnamic acids are too insoluble for the results to have much value for the purpose of this investigation: they also have the disadvantage of dissolving only very slowly; we have not studied their behaviour in the dry solvent.

TABLE I

Benzyl alcohol—formula weight 108.1.

In dry nitrobenzene:—

C.	D.	M.	x.	K.	γ.
1.577	0.930	114.5	1.059	4.02	0.879
2.694	1.502	119.9	1.109	5.11	0.805
4.120	2.152	126.5	1.170	6.53	0.730
5.762	2.794	134.6	1.245	8.23	0.658
7.396	3.352	142.4	1.318	11.31	0.612
9.028	3.852	149.9	1.387	14.90	0.548
11.36	4.468	160.6	1.486	22.91	0.491

In fully saturated nitrobenzene:—

C.	D.	M.	x.	K.	γ.
0.823	0.485	113.5	1.051	6.31	0.889
1.238	0.709	116.1	1.075	6.73	0.883
1.787	0.995	119.0	1.101	6.93	0.832
2.488	1.337	122.5	1.135	7.33	0.789
3.562	1.800	128.8	1.192	8.99	0.730
4.250	2.088	132.0	1.221	9.63	0.700
5.392	2.490	139.4	1.290	12.73	0.652
6.415	2.848	144.1	1.332	14.21	0.620
8.570	3.467	156.3	1.445	23.18	0.563
10.33	3.911	165.6	1.532	34.14	0.528

---

[1] J. Chem. Soc., **125**, 2219 (1924).

TABLE II

Iso-amyl alcohol—formula weight 88.1.

In dry nitrobenzene:—

C.	D.	M.	x.	K.	γ.
0.965	0.701	93.5	1.060	5.51	0.890
2.163	1.400	103.5	1.174	9.16	0.743
3.245	1.924	111.9	1.271	14.66	0.651
3.987	2.202	119.5	1.356	21.72	0.590
5.246	2.628	130.7	1.484	38.52	0.512
6.194	2.895	139.4	1.582	64.34	0.470
6.416	2.940	142.1	1.613	77.67	0.461
6.733	3.007	145.5	1.652	100.7	0.446
8.455	3.370	161.9	1.839	517.5	0.387
12.63	3.680	180.0	2.043		0.339

In partially saturated nitrobenzene:—

C.	D.	M.	x.	K.	γ.
0.521	0.386	91.0	1.033	5.05	0.870
1.377	0.911	99.7	1.132	10.65	0.816
1.602	1.051	101.5	1.152	11.16	0.794
2.341	1.426	108.6	1.232	15.39	0.708
3.480	1.923	118.7	1.347	23.57	0.600
4.601	2.303	130.0	1.475	41.60	0.526
6.117	2.722	145.1	1.647	105.8	0.448
6.754	2.843	153.1	1.737	210.3	0.420
8.245	3.167	166.7	1.892	1344.	0.370
10.14	3.429	188.3	2.137		0.320
11.45	3.615	201.0	2.282		0.294
14.75	3.932	236.7	2.686		0.245

In fully saturated nitrobenzene:—

C.	D.	M.	x.	K.	γ.
1.776	1.129	104.0	1.180	13.17	0.771
2.091	1.285	107.2	1.216	15.25	0.732
3.281	1.797	119.0	1.350	25.66	0.607
5.152	2.368	140.4	1.593	83.81	0.477
6.566	2.712	155.2	1.762	270.2	0.412
8.305	3.024	175.1	1.987	126900.	0.352
9.965	3.248	194.7	2.211		0.309
11.32	3.421	209.3	2.375		0.283
14.06	3.660	241.9	2.746		0.241

TABLE III

β-Naphthol—formula weight 144.1.

C.	D.	M.	x.	K.	γ.
In dry nitrobenzene:—					
0.737	0.348	144.5	1.003	0.442	0.989
2.134	0.989	145.6	1.010	0.597	0.967
2.861	1.310	146.7	1.017	0.793	0.955
4.927	2.197	148.0	1.027	0.729	0.926
6.095	2.680	148.7	1.032	0.711	0.911
7.459	3.220	149.9	1.040	0.758	0.894
In partially saturated nitrobenzene:—					
1.718	0.792	145.1	1.007	0.492	0.971
2.465	1.121	146.3	1.015	0.849	0.951
4.519	2.000	147.9	1.026	0.772	0.920
6.440	2.780	149.5	1.037	0.809	0.893
8.507	3.580	151.0	1.048	0.819	0.868
In fully saturated nitrobenzene:—					
2.002	0.910	146.0	1.013	0.833	0.967
3.256	1.452	147.2	1.021	0.870	0.935
4.032	1.778	148.1	1.028	0.936	0.919
5.267	2.270	150.4	1.043	1.185	0.896
6.901	2.903	151.9	1.054	1.170	0.869
8.061	3.343	152.8	1.060	1.216	0.849
8.760	3.579	154.5	1.072	1.321	0.839

TABLE IV

Phenyl-acetic acid—formula weight 136.1.

C.	D.	M.	x.	K.	γ. 1
In dry nitrobenzene:—					
1.126	0.363	211.6	1.555	431.5	0.47
3.629	1.069	228.9	1.682	351.7	0.290
4.289	1.242	231.7	1.703	354.7	0.263
5.426	1.557	232.8	1.710	304.7	0.246
8.288	2.323	234.8	1.726	231.3	0.207
10.52	2.913	235.0	1.727	187.1	0.185
13.41	3.655	235.5	1.730	153.1	0.172
In fully saturated nitrobenzene:—					
0.938	0.337	186.6	1.372	153.7	0.601
1.433	0.488	196.4	1.443	161.6	0.528
3.600	1.107	214.9	1.579	163.1	0.364
4.133	1.264	215.8	1.584	150.5	0.345
4.645	1.407	216.9	1.594	141.0	0.329
7.863	2.272	223.9	1.645	124.9	0.270
9.219	2.617	226.2	1.663	122.3	0.250
11.62	3.242	227.7	1.673	107.4	0.229
13.00	3.577	229.3	1.685	106.3	0.219

TABLE V

Propionie acid—formula weight 74.1.

In dry nitrobenzene:—

C.	D.	M.	x.	K.	γ.
0.380	0.238	109.2	1.474	400.6	0.459
0.952	0.536	121.0	1.632	487.7	0.303
1.837	0.960	129.1	1.743	648.0	0.221
2.885	1.439	134.2	1.811	886.2	0.178
4.172	2.033	135.8	1.834	821.2	0.151
6.073	2.885	137.1	1.850	733.5	0.128
6.266	2.952	138.1	1.864	881.0	0.126
6.713	3.132	139.0	1.875	1018	0.122
9.508	4.279	140.9	1.902	1905	0.106
In partially saturated nitrobenzene:—					
0.788	0.458	116.2	1.570	645.4	0.347
1.171	0.643	123.0	1.661	743.3	0.292
1.495	0.806	125.1	1.689	717.6	0.262
3.273	1.625	133.8	1.805	915.8	0.184
6.070	2.837	138.8	1.873	1227	0.137
8.026	3.620	142.2	1.919	2351	0.120
In fully saturated nitrobenzene:—					
0.793	0.450	117.8	1.590	208.7	0.396
1.396	0.762	122.0	1.646	164.6	0.304
3.031	1.532	129.7	1.751	143.5	0.217
4.973	2.352	136.5	1.842	788.4	0.172
6.958	3.162	139.8	1.887	1208	0.147
8.594	3.760	143.6	1.937	3585	0.133

TABLE VI

Benzoic acid—formula weight 122.1.

In partially saturated nitrobenzene:—

C.	D.	M.	x.
1.007	0.362	187.9	1.539
1.885	0.630	200.8	1.645
2.445	0.796	205.8	1.686
3.119	1.009	206.2	1.689
3.850	1.221	209.5	1.716
4.838	1.499	213.0	1.745
In wet nitrobenzene:—			
0.325	0.138	158.7	1.300
0.741	0.280	177.2	1.452
0.972	0.360	180.8	1.481
1.826	0.628	193.9	1.588
3.111	1.019	202.2	1.657
3.890	1.248	205.4	1.682

TABLE VII

Cinnamic acid—formula weight 148.1.

In partially saturated nitrobenzene:—

C.	D.	M.	x.
0.657	0.197	226.5	1.529
0.747	0.220	229.9	1.552
0.862	0.246	236.7	1.598
1.803	0.477	253.9	1.714
2.159	0.568	255.7	1.726
2.785	0.710	262.6	1.774
2.995	0.760	264.0	1.782

In fully saturated nitrobenzene:—

C.	D.	M.	x.
0.578	0.170	208.7	1.409
0.774	0.236	220.0	1.486
0.917	0.376	222.8	1.502
1.620	0.453	239.2	1.614
1.643	0.459	239.4	1.616
1.955	0 535	243.9	1.646
2.175	0.582	249.7	1.686
2.525	0.668	251.8	1.700
2.754	0.712	258.6	1.746
2.920	0.750	259.1	1.750
3.100	0.775	266.6	1.797

The results of Beckmann and Augustin[1] for cinnamic acid are in close agreement with ours; apparently the degree of moisture of their solvent was very close to our partially saturated solvent in the presence of Na_2SO_4, $o-10H_2O$: their figures for benzoic acid differ considerably from ours. Ampola and Carlinfanti[2] have measured the association of benzyl alcohol: their results are in as close agreement with ours as could be expected from the accuracy of their work. Boeseken and van der Eerden[3] have studied the association in nitrobenzene of cinnamic, benzoic, phenylacetic, and propionic acids, and ofamyl alcohol (a mixture of isomers): their results are so inconsistent that nocomparison is possible.

Conclusions

Auwers[4] came to the conclusion that associated substances could be divided into two classes, each of which was characterised by a definite type of concentration-association curve: this same division holds in nitrobenzene solution for the substances that we have examined, and would appear, from a study of literature, to be perfectly general. Our work shows that the two classes are also differentiated by the effect of moisture on their degree of association. The distinction between these two classes is illustrated in Fig. 1, in which the degree of association of one substance of each class in the wet and in the dry solvent is plotted against the concentration of the solution, expressed as mols per hundred grams of solvent.

---

[1] Z. physik. Chem., **60**, 385 (1907).

[2] Gazz., **26II**, 76 (1896).

[3] Rec. Trav. chim., **33**, 301 (1914).

[4] Z. physik. Chem., **30**, 300 (1899).

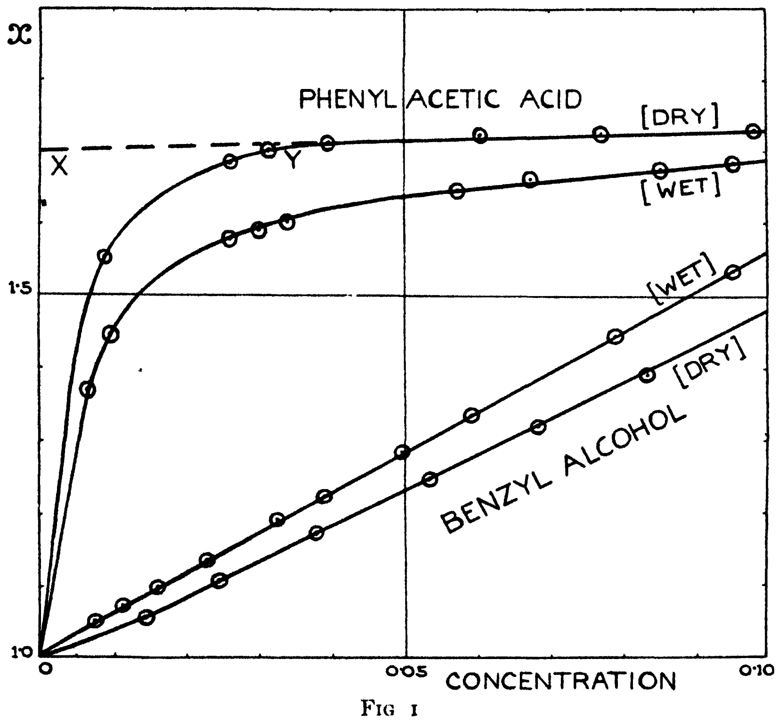


Fig 1

With the first class (class A), of which alcohols and phenols are typical examples, the degree of association increases steadily with concentration, and does not appear to reach a limit. These substances are more associated in the wet solvent.

With the second class (class B), of which acids are typical examples, the degree of association increases rapidly with concentration up to a point, beyond which it only increases very slowly: i. e., the degree of association seems to have a limiting value. With the two acids for which it has been found possible to measure the association to sufficiently high concentrations, this limit is approximately, but not exactly, 2. Substances of this class are more associated in the dry solvent, at any rate in dilute solution.

With one substance of this class (propionic acid) we have reached a point where the wet and dry curves intersect. It is probable from the direction of the curves that all the other substances of this class would behave in a similar manner at sufficiently high concentrations: in the figure the wet and dry curves of phenyl-acetic acid are obviously approaching each other at high concentrations.

Several observers, working with substances of class B, have overlooked the steep part of the curve in dilute solution, and have suggested that the association-concentration curve in dilute solution is of the type shown by the dotted line XY in Fig. 1—that is to say, the solute has an abnormal molecular weight even at infinite dilution (See, for example, Beckmann and Augustin (loc. cit.) on benzoic acid in nitrobenzene, Hentschel[1] on acetic acid in benzene. The question is discussed by Turner, "Molecular Association," p. 35 (1915)).

The second conclusion to be drawn from this work is that none of the solutes examined obey the law of mass action, with the possible exception of β-naphthol, which is so slightly associated, even at the highest concentrations, that it is hardly fair to draw any conclusions from it. That substances of class A do not obey the law is obvious from the form of the association-concentration curve. If association to double molecules is assumed, it is possible to calculate the mol fractions of single and double molecules (N_s and N_d) from the values of x given, and thence the equilibrium constant ($K = N_d/N_s^2$), the values for which are given in the fifth column of Tables I-V. These are not constant in any one series, and no better agreement is obtained by assuming the formation of triple or more complex molecules.

The fact that the law of mass action is not obeyed forces one to the conclusion that the assumption of association is not a complete explanation of the abnormality of these substances; it is also necessary to assume that for some unknown reason either the single molecules, the complex molecules, or both, do not form ideal solutions in nitrobenzene, that is to say, their active masses are not proportional to their concentrations expressed as mol fractions. If this is the case, it is not valid, except at infinite dilution, to deduce the molecular weights or degrees of association of associated substances from freezing points or any other related properties of their solutions: at best these quantities are a convenient measure of the abnormality of the solution.

Since association is not a complete explanation of the abnormal behaviour of these substances, and since the degree of association would appear to be an unmeasurable quantity, it is desirable to keep in mind the possibility that association does not occur at all. Whilst most organic substances containing an hydroxyl group are markedly abnormal from every point of view, there seems to be no definite evidence of the existence of complex molecules. Even the abnormal molecular weights of acids in the gaseous state have been shown to be largely due to an experimental error—neglect of an adsorbed layer of acid on glass surfaces.[1] Tyrer's criticism of the method of deducing degrees of association from the temperature coefficient of molecular surface energy[2] seems unanswerable, and it is probable that abnormal values of this constant (and, indeed, most of the abnormal properties of these compounds) are due, not to association, but to their polarity,[3] or intramolecular ionisation as it was originally called by Thomson.[4] Baker's observations of the properties of certain dry liquids,[5] most of which were typically normal compounds, merely proves that these liquids are mixtures, but not necessarily associated, as is usually assumed. There are, for example, grounds for belief that benzene is a mixture of tautomeric forms of the same molecular weight.[6] The results obtained by Baker and McBain[7] for the adsorption of toluene and acetic acid on charcoal, which they attribute to the existence of acetic acid as double molecules, can be explained equally well by the assumption that a molecule of toluene occupies twice as much space as does one of acetic acid on the surface of charcoal. The only satisfactory chemical[8] evidence of association is for substances with uneven numbers of electrons in the molecule, such as NO_2, $(C_6H_5)_3C$, and I.

---

[1] Z. physik. Chem., 2, 306 (1888).

Calculation of Activities

As has been pointed out above, the degree of association is, at best, a convenient measure of abnormality—it is, moreover, an unsatisfactory measure: since "associated" substances do not form ideal solutions, the degree of association will depend on the experimental means employed to determine it. (This, it will be noticed, is characteristic of the degree of association.) A much more suitable measure of the abnormality is the activity, since this should be independent of the experimental means used to determine it, provided that they have the necessary accuracy. We have therefore calculated activity coefficients from our freezing point data.

These calculations of activities are offered with reserve, as preliminary results, for the thermodynamic data for nitrobenzene are not free from uncertainty: also, calculation of activities of solutes involves extrapolation to infinite dilution, and is therefore liable to serious error if accurate data for dilute solutions are lacking: the Beckmann method is known to be unsuitable for accurate work in dilute solutions, and in our experimental work we have paid little attention to this region: when more accurate data are available, it may be necessary to multiply our results for any one series throughout by a constant. This uncertainty applies more particularly, to substances of class B, and to results for the moist solvent. We are at present engaged in trying to confirm some of these activities by an independent method.

---

[1] Drucker and Ullmann: Z. physik. Chem., **74**, 567 (1910).

[2] Z. physik. Chem., **80**, 50 (1912).

[3] Hildebrand: "Solubility" American Chemical Society Monograph Series, (1924).

[4] Phil. Mag., (6) **27**, 757 (1914).

[5] J. Chem. Soc., **121**, 568 (1922).

[6] Ingold: J. Chem. Soc., **121**, 1133 (1922).

[7] J. Am. Chem. Soc., **46**, 2718 (1924).

[8] There is strong evidence from band spectra that some elements, such as helium, mercury, and sodium, do form complex molecules (He_2, Hg_2, Na_2) in the gaseous state, though these substances are among the most normal gases known to chemists. There is, as yet, no evidence as to whether these double molecules carry an electric charge or not, or whether their existence is probable under normal conditions.

The method of Lewis and Randall[1] was employed: the activity of the solvent (α_1) is connected with the freezing point depression (θ, which for the dry solvent is the same as D in our tables) by their equation XXIII-16. Taking the latent heat of fusion of nitrobenzene to be 22.46 cal.,[2] a value which is in excellent agreement with our molecular weight determinations of normal substances,[3] and taking the difference of the specific heats of solid and liquid to be 0.02 cal.,[4] this equation becomes:—

$$d \ln \alpha_1 = d\,\theta\,(-0.01785 - 0.000112\,\theta). \qquad (1)$$

If m is the number of mols solute, calculated from the formula weight, per mol of solvent, their equation XXII-19 becomes:—

$$d \ln \alpha_2 = \frac{-d \ln \alpha_1:}{m} \qquad (2)$$

where α_2 is the activity of the solute. Combination of these two equations leads to the equation:—

$$\ln \frac{\alpha_2}{m} = \int_m^0 -j\ d \ln m - j\ + \int_m^0 0.000112\,\frac{\theta\,d\theta}{m} + K, \qquad (3)$$

$$\text{where } j = 1 - \frac{0.01785\,\theta.}{m}$$

The two integrals can be evaluated graphically; K, the integration constant, is zero (with the dry solvent).

When dealing with the moist solvent, it is convenient to regard the depression of freezing point as taking place in two stages: first, by the addition of water, until the depression is D_w: in the second stage the activity of the water is kept constant, since the solvent is in contact with free water or a salt hydrate pair, and the freezing point is further depressed by an amount (D) through the addition of C grams of solute per 100 grams of nitrobenzene. Equation (1) is valid, provided that θ is put equal to $D+D_w$: for partially and fully saturated nitrobenzene the values of D_w are 0.323° and 0.511° respectively.[5] So long as the activity of the water is kept constant, equation (2) is true. Equation (3) is therefore valid, but the integration constant is no longer zero, since j is infinite when m is equal to zero. The only way of overcoming this difficulty that we can suggest, is to choose an arbitrary value of K such that the value of $\ln \alpha_2/m$ at infinite dilution, obtained by extrapolation, is zero.

---

[1] "Thermodynamics" (1923).

[2] Meyer: Z. physik. Chem., **72**, 225 (1910).

[3] J. Chem. Soc., **123**, 2037 (1923); **125**, 2219 (1924).

[4] Tammann: "Kristallisieren und Schmelzen", p. 228 (1903).

[5] J. Chem. Soc., **123**, 2037 (1923).

The values of α_2/m obtained in this way, for the wet and dry solvents, have been multiplied by (m+1), giving the activity coefficient ($\gamma = \alpha_2/N_2$, where N_2 is the mol fraction of solute): values of this are given in the sixth columns of Tables I-V. Values at round concentrations, obtained by interpolation, are given in Table VIII, for solutions in dry and in fully saturated nitrobenzene. Activities for solvents in the dry solvent should be comparable with those calculated from vapor pressure measurements; those in the wet solvent with activities from distribution experiments.

TABLE VIII

Activity coefficients at round concentrations.

Mol fraction.		.01	.02	.03	.05	.07	.10	.13
Substance.		Activity coefficient.						
Benzyl alcohol	(dry)	.93	.87	.81	.71	.63	.53	
	(wet)	.91	.83	.77	.68	.59	.49	
Iso-amyl alcohol	(dry)	.91	.83	.74	.61	.51	.40	.33
	(wet)	.90	.81	.72	.57	.46	.36	.29
b-naphthol	(dry)	.98	.96	.94	.90	.87		
	(wet)	.97	.95	.92	.87	.82		
Phenyl-acetic acid	(dry)	.47	.36	.29	.24	.20	.18	
	(wet)	.57	.44	.37	.30	.26	.22	
Propionic acid	(dry)	.36	.27	.22	.17	.15	.12	.11
	(wet)	.49	.32	.27	.21	.18	.15	.13

Summary

1. The depression of the freezing point of dry, wet, and partially saturated nitrobenzene by benzyl and iso-amyl alcohols, β-naphthol, and phenyl-acetic, propionic, benzoic, and cinnamic acids have been measured.

2. "Associated" solutes can be divided into two distinct classes: alcohols and phenols are apparently more associated in the wet solvent, and their degree of association seems to increase without limit as the concentration is increased: organic acids are apparently more associated in the dry solvent, and the degree of association approaches a limit.

3. The change in the degree of association with concentration does not obey the law of mass action. The consequences of this fact are discussed.

4. Preliminary calculations of the activities in dry and in wet nitrobenzene have been made.

We are grateful to Mr. L. J. Hudleston for advice on some points in thermodynamics. One of us (F. S. B.) desires to acknowledge his indebtedness to the Board of Scientific and Industrial Research for a maintainance grant (1923-1925), and to this College for the award of a Garrod Thomas research Scholarship (1925-1926).

Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth,
Wales.
Dec. 21 (1925).

THE SCATTERING OF LIGHT BY AQUEOUS SODIUM SILICATE SOLUTIONS

BY P. B. GANGULY

The object of the following investigation was to compare the light-scattering powers of a series of aqueous solutions of "sodium silicate", containing different concentrations and different ratios of SiO_2 to Na_2O, in the hope that such a comparison would provide some evidence concerning the presence in the solutions of colloidal complexes or micelles. When a beam of light is passed through the solution, the colloid particles will scatter light in addition to that scattered by the molecules and ions, and this scattering effect will be much more intense. Another object of the present investigation was to ascertain whether there is a marked increase of light scattering when solutions of equivalent Na_2O or SiO_2 concentration, but containing increasing quantities of SiO_2 are compared.

For particles of low light absorption the intensity, I, of the scattered light is given according to Lord Rayleigh by the expression $I = Knr^6/\lambda^4$ where k is a constant depending on the intensity of the incident beam, the refractive indices of the liquid and the disperse phase and the angle of observation of the scattered beam, n the number of particles per unit volume, r their radius and λ the wave-length of the incident light. If c be the concentration (mass per unit volume) and ρ the density of the particles of the disperse phase, $c = 4/3\pi r^3 n\rho$, and therefore $I = kcv/\rho\lambda^4$, where v = volume of a particle. Thus the intensity of the scattered light is directly proportional to the concentration of the disperse particles and to the volume of each particle. A similar expression for substances with a higher light absorption has been given by Mie[1].

The applicability of the Rayleigh formula to a colloidal solution was tested by Mecklenburg[2] who was working with Odén's sulphur sols found that only smaller particles, of sizes between 5 and 93 $\mu\mu$, scattered light in accordance with the above formula. More recently Bechhold and Hebler[3] examined the light scattered from $BaSO_4$ particles in a Klienman nephelometer and found that the Rayleigh equation was applicable to particles of size up to 800 $\mu\mu$ but not beyond.

In the present work the relative intensities of the scattered light were not quantitatively determined, the various solutions being graded by comparison against a standard turbid medium in the instrument devised by Kingslake[4]. This consists of two tubes which are carried by metal sheaths mounted in vertical slides, a parallel beam of light being passed through the tubes, one of which contains the solution under examination and the other some suitable opalescent medium as a standard. With the help of a Nutting prism, the lights scattered from the two tubes are brought into juxtaposition, and by sliding the standard tube up and down the fields can be matched in brightness. The standard opalescent medium used in the present experiments was a 2 per cent gelatine gel containing finely disperse barium sulphate (0.05 gram per 100 cc.). By employing very pure gelatine and introducing a little xylene on the top of the tube (kept securely stoppered) the standard can be preserved from change. Proceeding in this way, the light scattered from any given silicate solution can be matched in brightness by the light scattered from some particular thin "slice" of the standard medium. The latter was calibrated by comparing it against aqueous alumina sols of different concentrations, these sols being prepared by Graham's method[1]. The water used for diluting the original alumina sol and for all subsequent purposes was rendered as free from dust as possible by filtration through a Zsigmondy membrane filter. Examination in an ultramicroscope showed that such water was fairly free from suspended particles. The calibration curve is shown in Fig. 1 in which the scale reading of the standard is plotted against the concentration of the alumina sol (in grms. alumina per 100 cc.).

---

[1] Ann. Physik, **25**, 377 (1908).

[2] Kolloid-Z., **16**, 97 (1915).

[3] Kolloid-Z., **31**, 70 (1922).

[4] Trans. Optical Soc., (2) **26**, 53 (1924-25).

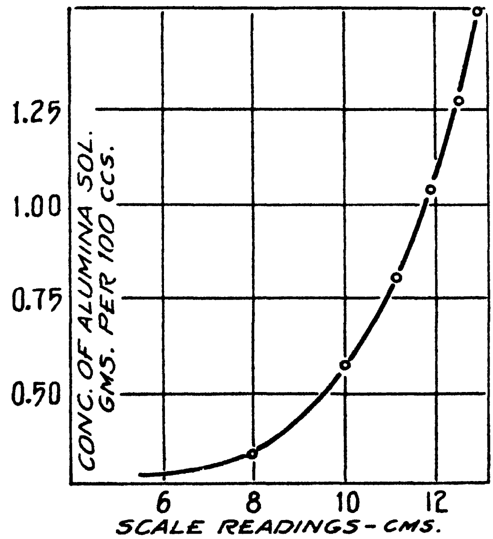


FIG. 1

Eight technical silicate solutions varying in the molar ratio SiO_2/Na_2O from 2.0 to 4.2 were obtained from Brunner, Mond & Co. In order to free these solutions from suspended coarse particles, they were allowed to stand many months in stoppered bottles, after which the supernatant solutions were removed and further freed from such suspensions by centrifuging and by filtration through Zsigmondy "analytical" membrane filters. By suitable dilution with dust-free water these eight solutions were compared at a constant SiO_2 concentration of 2.5 molar. The results are shown in Table I.

---

[1] Phil. Trans., **151**, 183 (1861).

TABLE I

Technical Silicate Solution	Molar Ratio SiO_2/Na_2O	Scale reading of standard	Corresponding concentration of equivalent alumina sol. (grms. per 100 cc.)
A	4.2	12.9	1.35
B	3.95	12.4	1.12
C	3.8	11.9	0.93
D	3.3	11.3	0.75
E	3.0	8.3	0.27
F	2.9	8.6	0.294
C	2.5	9.2	0.36
H	2.0	8.5	0.285

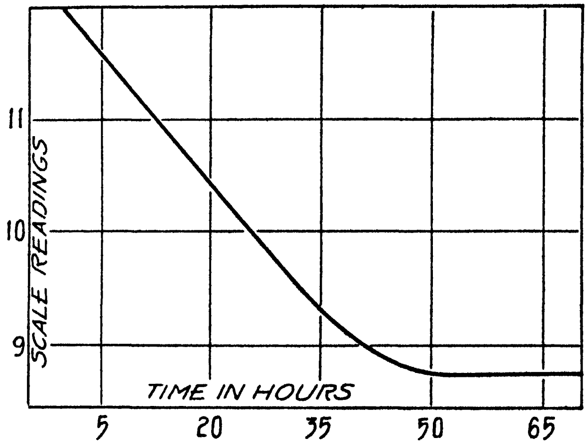


FIG. 2

It will be seen that between the ratios 2.0 and 3.0 there is not much change in scattering power, and no regular increase. Between ratios 3.0 and 3.3 there is a rapid increase in scattering power, and between 3.3 and 4.2 a steady increase with increase of ratio of SiO_2 to Na_2O. The corresponding concentrations of the alumina sols possessing equal scattering powers show that the observed increases in scattering power correspond in all probability to increasing contents of colloidal particles or micelles in the silicate solutions or to increasing size of those already present. Probably both effects occur.

As the technical solutions may vary in mode of preparation, it was considered likely that more comparable results would be obtained by starting with the technical solution of highest ratio (A) and preparing, by addition to it of suitable quantities of water and alkali, a series of solutions of varying ratio of SiO_2 to Na_2O. Two such series were prepared, all the solutions being 2.5 molar with respect to SiO_2 in one series and 2 molar with respect to Na_2O in the other.

In order to investigate the time required by such solutions to reach a state of equilibrium, 35.04 grms. of the 4.2 ratio silicate solution were mixed with 2.608 grm. of NaOH and sufficient water to make up the volume to 50 cc. The resulting solution is 2.5 molar with respect to SiO_2 and the ratio of silica to alkali in it is 2. This solution was examined in the nephelometer from time to time, the results being shown in Fig. 2. This curve exhibits clearly the very interesting and marked decrease of scattering power with time, indicating that colloidal complexes or micelles are being gradually converted into simpler colloidal units, or partly into simple molecules and ions. It will be seen from Fig. 2 that equilibrium was attained in fifty hours. All solutions used in these experiments were therefore left for three days before being examined in the nephelometer. The NaOH solutions were prepared from metallic sodium, and allowed to stand in closed vessels for several weeks, after which the top layer was siphoned off for use. The results are shown in Tables II and III.

TABLE II

Silicate Solutions 2.5–molar with respect to SiO_2

Molar Ratio SiO_2/Na_2O	Scale Reading	Concentration of corresponding Al_2O_3 sol.
4.2	12.9	1.34
4.0	12.5	1.14
3.8	12.2	1.025
3.5	11.3	0.75
3.0	9.7	0.42
2.7	9.3	0.375
2.5	9.1	0.35
2.2	8.8	0.31
2.0	8.6	0.294
1.7	8.1	0.25
1.5	7.6	0.225
1.0	7.0	0.187

TABLE III

Silicate Solutions 2–molar with respect to Na_2O

Molar Ratio SiO_2/Na_2O	Scale Reading	Concentration of corresponding Al_2O_3 sol
4.2	13.2	1.52
4.0	13.0	1.4
3.8	12.6	1.19
3.5	11.8	0.9
3.3	10.8	0.65
3.0	9.9	0.45
2.5	9.1	0.35
2.0	8.1	0.25
1.5	7.0	0.19
1.0	6.1	0.15

All the sodium silicate solutions scatter light very considerably, the scattering power being altogether of a different order from that of ordinary molecular solutions. Thus even very concentrated solutions of sodium hydroxide, when properly freed from suspended particles, give scale readings on the standard lying between 2 and 4, whilst for the silicate solutions the readings lie between 8 and 13. In this connection it must be recollected that the scattering power increases rapidly with the scale reading of the standard, as may be seen from Fig. 1.

The results given in Tables II and III are shown graphically in Fig. 3.

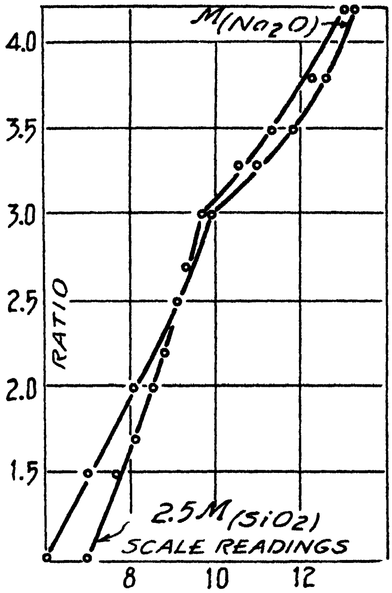


Fig. 3

Both curves show apparent breaks at the 3 ratio solutions, the scattering power at this point beginning quite sharply to increase more rapidly with increase of the molar ratio of SiO_2 to Na_2O. A similar result emerged from the comparison of the scattering powers of the technical solutions. There is therefore very good evidence that after the ratio 3 is passed the number or the size of the colloid particles or micelles begins sharply to increase more rapidly with increase of the ratio.

The various technical silicate solutions have been examined in a slit ultramicroscope and the particles counted. It has already been stated that the water used for dilution purposes though filtered through a membrane filter was not optically void. When allowed to stream through the apparatus it showed a light cone, but when the flow was stopped only a few particles could be seen in the field of vision. Table IV gives the average counts for the technical silicate solutions, all the solutions being $\frac{1}{8}$-molar with respect to SiO_2.

TABLE IV

Solution	Molar Ratio SiO_2/Na_2O	Average number of visible particles per cc.
A	4.2	3.4×10^9
B	3.95	1.9×10^9
C	3.8	1.8×10^9
D	3.3	1.5×10^9
E	3.0	1.17×10^8
F	2.9	1.28×10^8
G	2.5	1.34×10^8
H	2.0	1.05×10^8

If the particle concentration be plotted against ratio, as given in Fig. 4, the resulting curve shows that there is a very sudden and rapid change in the rate of increase of particle concentration with ratio as the ratio 3 is exceeded. This result is in agreement with the measurements on light scattering power.

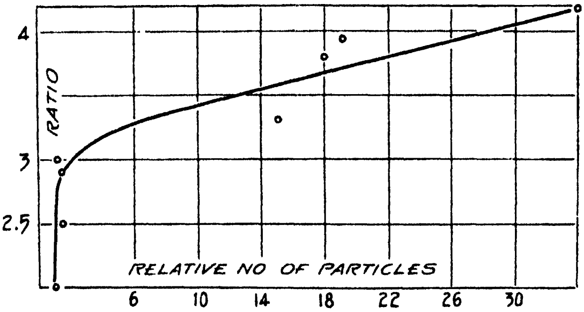


FIG. 4

Summary

1. Aqueous soldium silicate solutions of varying ratio of silica to alkali have been examined as to their relative scattering power for white light. The scattering power is very much greater than that of ordinary molecular solutions, and the rate of change of this property with increase of ratio undergoes a sudden increase after the ratio 3 is exceeded.

2. The silicate solutions have been examined in a slit ultra-microscope and the average number of visible particles per cc. determined. The results show that when the ratio 3 is exceeded there occurs a very rapid increase in the number of particles per cc.

3. It is inferred that the sodium silicate solutions contain colloidal aggregates or micelles, that these increase in concentration or size (or both) as the ratio of silica to alkali increases, and that the amount of colloidal matter increases rapidly with increase of this ratio after the ratio 3 is exceeded.

In conclusion the author wishes to express his thanks to Professor F. G. Donnan, for his many valuable suggestions and for his kind interest in this work.

The William Ramsay Laboratories of
Physical and Inorganic Chemistry,
University College,
London.
Feb. 9, 1926.

A LABORATORY LATEX[1]

BY HSI-CHING CHEN

The raw material which forms the basis of the rubber industry is a gum imported from the tropical regions of Asia, Africa, and America. It is obtained in the form of an aqueous emulsion or latex secreted in the cambium of certain trees and creepers. From this latex the rubber is obtained as a tenacious, springy, self-adhesive mass by methods of coagulation which vary somewhat widely with botanical origin, local custom, and other factors. An average analysis of rubber latex shows it to contain the rubber hydrocarbons as it's chief constituents to the extent of 25-40% rubber with varying amounts of resins, sugars, proteins, and mineral salts, the balance being water. In plantation rubber from Ceylon the rubber content is usually put at about 40% and the water content at about 55%. The globules in the emulsion are said to be about 3μ in diameter for *Ficus elastica*, 2μ for *Hevea brasiliensis* and less than 1μ for *Funtumia elastica.*

While there is no reason to suppose that the rubber latex differs in principle from other emulsions, there is a wide-spread belief that the rubber latex is in a class by itself because it is apparently the only emulsion with which rubber chemists have ever worked. It seemed desirable therefore to see whether one could make a substitute latex which could be studied easily in the laboratory and which would duplicate many or perhaps most of the reactions of the real latex. Evidently the first requisite for a laboratory latex is that the emulsified material should be liquid but should solidify when the emulsion cracks. This was easy to do, though the method is not that adopted by nature in the rubber latex. Cazeneuve[2] has shown that acetaldehyde liquefies camphor and that the resulting liquid floats on water. By emulsifying the mixture of camphor and acetaldehyde, we can get an emulsion. When the emulsion cracks, the acetaldehyde will evaporate leaving solid camphor behind.

The acetaldehyde used in these experiments was made from paraldehyde by distillation from concentrated sulphuric acid. Only freshly prepared samples were used. Since the camphor could not be ground, one gram of it was cut into small pieces and placed in a test-tube into which was run 4cc H_2O and 2cc aldehyde. Two liquid layers are formed with the camphor solution floating on top. About 0.02 grams of sodium oleate were added and the whole shaken intermittently[3] until an emulsion was formed.

---

[1] Based on a thesis for the M.Sc. degree in Chemistry presented to the Faculty of the Graduate School of Cornell University in May, 1922.

[2] Bull. (2) **36**, 650 (1881).

[3] Briggs: J. Phys. Chem. **24**, 120 (1920).

The methods of coagulation of the rubber may be classified[1] as follows:—

1. Smoking: by injecting steam and acid smoke. Smoking with Urucury nuts in the lower Amazon regions and with hard woods above Manaos. The smoke is said to contain acetone, acetic acid, creosote, and tarry matters.

2. Evaporation. The latex dries to 'scrap' if allowed to run down the bark. It may be poured into saucer-shaped stumps in which case the wood soaks up the water or the water evaporates into the air.

3. Boiling. This method of coagulation can be used for Castilloa, Ficus, and Funtumia latices but does not work satisfactorily with Hevea.

4. Dilution. This causes coagulation with Castilloa, Landolphia, and Funtumia but not with Hevea.

5. Addition of acids, salts, alcohol, acetone, etc. Over 90% of the plantation rubber latex is coagulated with acetic acid in some form. Alcohol and acetone give an admirable coagulation but are too expensive. Hübener points out that alcohol works only in presence of salts which is exactly what one would expect from what one knows about negatively charged sols[2]. Whitby[3] states that dialyzed latex is not precipitated by methyl, ethyl, or amyl alcohol but is by acetone.

6. Beating, churning, and centrifuging. Beating worked with Manihot rubber. Beadle and Stevens[4] state that churning or shaking has no effect on normal Hevea latex. "If, however, sufficient of a coagulant be added to produce creaming and flocculation on standing, the effect is hastened and the flocks are more dense if the liquid be shaken vigorously. It is natural to suppose that with shaking or churning we have merely the mechanical effect of bringing the aggregates into frequent contact with each other, causing them to adhere and join up, forming larger and more compact aggregates." Centrifuging[5] works well with Castilloa (3μ), not very well with Hevea (2μ), and not at all with Funtumia ($\langle 1\mu$), which is exactly what one would expect so far as creaming is concerned.

In order to duplicate to some extent the South American method of smoking, acetic acid and steam were distilled into the emulsion. Cracking and solidification occurred. Of course this is really coagulating with hot acetic acid; but people have always made the distinction.

If the laboratory latex is allowed to evaporate, the emulsion cracks and solid, white camphor is obtained as the acetaldehyde passes off. Slight warming speeds up the cracking considerably. When the laboratory latex is boiled, the emulsion breaks down. The differences observed with different natural latices are undoubtedly due to variations in the amount and nature of the protecting colloid. When the laboratory latex is diluted with about 10 cc of water, the emulsion is destroyed. Freezing[1] also gives camphor. With more emulsifying agent the emulsion would not break down on dilution or on freezing and would then behave like the Hevea latex.

---

[1] Clouth: "Rubber, Gutta Percha and Balata," 66 (1903); Spence: "Lectures on India Rubber," 25 (1909); Schidrowitz: "Rubber," 127 (1911); Hübener: Kolloid-Z. **16**, 5 (1915).

[2] Bancroft: Rec. Trav. chim. (4) **3**, 733 (1923); Bancroft and Gurchot: J. Phys. Chem. **28**, 1279 (1924); Gurchot: **30**, 83 (1926).

[3] "Plantation Rubber and the Testing of Rubber," 34 (1920).

[4] Eighth Congress Applied Chemistry, **9**, 37 (1912).

[5] Beadle and Stevens: Kolloid-Z. **13**, 210 (1914).

It seemed unnecessary to make cataphoresis experiments because the liquid drops would certainly go to the anode in a soap solution. Centrifuging seemed also to be a mere waste of time. It is evident that the laboratory latex duplicates the real one in many respects. One could give additional stability against heating and evaporation by using a less volatile liquid than acetaldehyde; but it would take correspondingly longer before the camphor solidified. Some people may be horrified by the use of soap; but it is perfectly possible to substitute any other protecting colloid so long as it does not reverse the emulsification. It would also be an easy matter if one wished to duplicate or simulate the bacterial action which occurs in the natural latex.

Summary

Practically all the reactions of a rubber latex may be duplicated with an emulsion made up of one part camphor, four parts water, 0.02 parts sodium oleate and 1.5 parts acetaldehyde. On coagulation the camphor is obtained as a white solid. The following methods of coagulating rubber have been duplicated with the laboratory latex: smoking, evaporation, boiling, dilution, and addition of acetic acid, oxalic acid, tannic acid, tartaric acid, formic acid, citric acid, hydrochloric acid, sulphuric acid, hydrofluoric acid, alum, and alcohol. No coagulation was obtained with acetone or phenol; but this could perhaps have been secured if another emulsifying agent had been used.

I wish to extend my thanks to the various members of the staff of the Department of Chemistry for help which I have received and I wish particularly to thank Professor W. D. Bancroft, who suggested the investigation and whose kindly interest has assisted me over many difficulties.

Cornell University.

---

[1] Zsigmondy-Spear: "The Chemistry of Colloids," 8 (1917).

NEW BOOKS

A Dictionary of Applied Chemistry. *By Sir Edward Thorpe. Vol. VI. Revised and enlarged edition. 24 × 16 cm; pp. viii+791. London and New York, 1926. Price: $20.00.* This is the next to the last volume of the series and has been put through the press by H. Forster Morley. Among the interesting topics are: saccharin, safflower, sand, sandstone, saponification, sealing wax, selenium, sewage, shellac, silicon, silica, silk, silver, smoke, soap, sodium, soils, solder, solubility, soluble or water glass, solution, soya bean, specific gravity, spectroscopy, starch, steam, stearin, strontium, sublimation, sugar, sulphide dyes, sulphur, sulphuric acid, synthetic drugs, tallow, tannins, tantalum, tartaric acid, tea, tellurium, terpenes, and tetralin.

"The prevailing view that, except for its action on the organs of taste in the mouth, saccharin is an inert substance having no action on organs and tissues, is not tenable. Acting in the mouth, it decreases appetite, gastric secretion, and peptic digestion. Acting in the small intestine, it decreases absorption; on the erythrocytes, it decreases haemolysis. These actions cannot be explained by the osmotic factor. Saccharin in the blood, in proportion to its concentration, passes into the lymph, cerebrospinal fluid, saliva, tears, and mammary secretion," p. 3.

Safflower must be almost the only substance which is purified by dyeing cloth with it and then extracting the dye from the cloth, p. 7. "To obtain carthamin, safflower is well washed with slightly acidified water to remove the yellow colouring, then it is steeped for some time in a cold dilute solution of sodium carbonate. If the alkaline solution be now acidified with acetic or tartaric acid the carthamin is precipitated in so finely divided a condition that it cannot be collected successfully. This difficulty is obviated, however, by making use of the fact that carthamin is readily attracted and removed from its acidified solution by cellulose. Hence bleached cotton is immersed and moved about in the alkaline solution which is at the same time acidified gradually with tartaric or citric acid.

"In this manner the carthamin is precipitated slowly and is attracted at once by the cotton which thus becomes dyed red. After washing the dyed cotton with slightly acidified water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate, which is now in a purer and more granular form."

Under saponification, p. 41, the use of one percent of lime is cited as a case of catalysis whereas there is undoubtedly a formation of a water-in-oil emulsion. "Shakudo is an alloy consisting essentially of copper and gold, which is used in Japan for the manufacture of objects of art, and is colored by treatment with aqueous solutions containing copper sulphate and acetate. The coloration is due to the production of a layer of cupric oxide, the tint being determined by the thickness of the layer," p. 79. "Schaum and Lang state that for transmitted light the diameters of the particles of colloidal silver associated with the following colours are: yellowish-orange 60μ; orange-red 90μ; purple 120μ; violet 150μ; and bluish-green 180μ," p. 120.

"The character of smoke varies with its source, and in most cases the nose is able to detect the character of the burning material from the smell of the condensing vapours in the smoke, so that tobacco smoke, coal smoke, wood smoke, the smoke from green vegetable matter, rags, animal matter, or gunpowder have such distinctive characteristics that the sense of smell differentiates at once between them.

"The form of smoke which is, perhaps, the most injurious, and to which we are most, accustomed, is that produced by the use of bituminous coal as a fuel for manufacturing and domestic use, and which, with the growth of the population of the country and the prodigal methods of using the fuel, has created in our large towns atmospheric conditions that are little short of a national scandal.

"When in the thirteenth century bituminous coal was first used for fuel purposes, the smoke to which it gave rise roused such indignation that a decree was passed in 1306 forbidding its use; but fuel had to be found, and the supply of timber proving insufficient, attempts were made once more to introduce it, but again public opinion led to its banishment during the reign of Queen Elizabeth. The third attempt, however to bring it into use proved successful, and slowly the consumption increased, until the last century saw coal established firmly, not only as a fuel for domestic consumption, but also as a great source of power; and it was the possession of great stores of the fuel that gave England her commercial supremacy," p. 138.

"The double melting-point of tristearin is attributed to the existence of two modifications the more stable of which melts about 71.6°-72.2°, and the instable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the instable form (about 55°). . . . On seeding liquid tristearin with the stable modification above 60°, solidification takes place without the formation of the instable form, but the latter is apparently always produced after seeding, even with the stable form, at temperatures below 56°," p. 400. Apparently twenty-five years is not sufficient for organic chemists to master the theory of two modifications occurring in the melt.

"Owing to our lack of knowledge concerning the physiology of sleep and possible chemical processes that take place, we are equally ignorant of the exact manner in which sleep is produced by hypnotics. In effect, we must distinguish between narcotics (represented by opium), which produce unconsciousness by intoxication, and the true hypnotics (represented by chloral), in which the sleep is apparently normal. In view of the fact that the sleep produced by the opium class is often attended with undesirable by-effects, and that during their prolonged administration the element of habituation must always be considered, they have been reserved for cases of insomnia due to severe pain, and have been largely replaced in other forms of sleeplessness by the synthetic hypnotics. While this latter class approach the normal conditions, yet the ideal hypnotic remains to be discovered. This must act upon the nerve centres, followed later by the most automatic and stable centres, avoiding any profound influence on the respiratory or circulatory centres. Elimination must be rapid and complete, leaving no trace of cumulative or secondary action such as digestive disturbances, headache, etc. The hypnotic effect of the aliphatic hydrocarbons, developed through the introduction of hydroxyl groups (alcohols), is well known. That the hydroxyl serves no further purpose than that of an anchoring group is proved by the inert properties of the polyhydric alcohols. That the ethyl group produces a profound hypnotic effect, as in alcohol, is further demonstrated by the decomposition of chloral in the blood to trichlorethyl alcohol, and the necessary presence of alkyl groups in the most important classes of hypnotics. The introduction of the ethoxyl group into caffeine imparts a narcotic effect. It can be said in general that the alkyl groups, more especially the ethyl, possess a distinct sedative action upon the nervous system. The methyl group generally eliminates or diminishes hypnotic action when associated with an ethyl or propyl group; the propyl radicle with other higher radicles increases the intensity and also toxicity, while their corresponding *iso* groups generally diminish it. Sulphur replacing oxygen contributes to toxicity. The alkyl radicles do not carry hypnotic or sedative action under all conditions; it is only the association of certain groups or nuclei or their structural environment that determines this action. The presence of a sulphonic or carboxyl group inhibits physiological action, and diminishes toxicity. Another factor is insolubility, that is, failure to break down in the system; thus tetronal, which, theoretically, should possess a more profound hypnotic action than trional, is practically inert. A further insight is gained on studying the groups," p. 618.

"Antiseptics are chemicals which have the power, in small quantities, to prevent infection or to arrest the multiplication of bacteria, and should be free from harmful action upon the human organism. Disinfectants destroy bacterial life and the noxious properties of putrefactive or fermentative products. Usually, small quantities of these chemicals are antiseptic, and large amounts disinfectant, in their effects.

"The great variety of bacterial life, the kind, state, extent, composition, quantity, and condition of the associated matter, together with the difficulty of fixing, inhibiting and sterillising of disinfectants makes the subject of standardisation of disinfectants perplexing and difficult. An ideal disinfectant must be able to destroy bacteria, be harmless to the human organism, penetrative, free from local irritation, toxic action and disagreeable odour. Very few, if any, of the disinfectants are adapted for universal use because of the great variety of conditions presented, hence each product is adapted for some special field of work.

"Intestinal antisepsis is not attainable,because if the antiseptic were sufficiently powerful to destroy bacteria it must necessarily exhibit a toxic action on the human system. However, in certain lines, this class of antiseptics serves admirably in inhibiting the development of milder types of bacteria and neutralising the action of toxins in infections of the respiratory and urinary tracts. Combinations of bismuth and various antiseptics have become popular in treatment of intestinal disturbances due to fermentative changes or infection. To these must be added various compounds of beta-naphthol," p. 624.

Wilder D. Bancroft

Explosifs, Poudres, Gaz de Combat. *By Paul Pascal. 25 × 16 cm; pp. viii+296. Paris: J. Hermann, 1925. Price: 35 francs.* This book is based on lectures given at Lille, and the author implies that, for military reasons, he has not told all that he knows. The book is divided into four parts: explosion and detonation; manufacture of explosives; explosive mixtures and propellants; war gases.

There are some rather interesting paragraphs, p. 7, on the situation after the war started. "We had to evacuate the powder factory at Esquerdes near St. Omer when the drive for the Channel began, and had to start over again in the factories of the Southwest. The loss of our coke ovens in the North increased the shortage of hydrocarbons. It was necessary to import benzene and to extract the aromatic hydrocarbons from Borneo petroleum. Our black-powder factories were used to manufacture schneiderite and everywhere new factories were built which utilized the ammonium nitrate from Norway to supplement the stocks of melinite received from America. It was because of this production that it was necessary to install factories for the production of synthetic ammonia at Angoulême, Bassens, Borgues, and elsewhere.

The field of explosives was the one in which the really chemical effort was most serious. It was necessary to use new or more effective methods; the manufacture of synthetic phenol increased from six hundred to three hundred and seventy thousand kilograms per day and we had to rely on outside for only a negligible amount of this compound. The output of the French factories, supplemented by those of the confiscated German dye works, enabled us to meet the most urgent needs. Toulouse even supplied Italy when she first came in; we supplied the Balkans throughout the whole war and the Americans in 1917-1918."

It is possible to eliminate almost completely the flare-backs and to decrease the flash from the gun by adding alkaline salts to the charge, p. 82. To prevent the propagation of explosion flames in mines, planks are placed overhead on which finely divided cinders are piled. The explosion shakes down the dust, p. 88.

By fractional precipitation of nitro-cotton from acetone by means of toluene, it is possible to separate a two percent sol having a viscosity of 0.1 into two portions, one having a viscosity of 0.6 and the other of 0.007, p. 103. "Cotton is an expensive form of cellulose and also an exotic material and is hard to secure when there is a submarine war on. We have hoped to decrease these difficulties by growing it in our African colonies; but wood constitutes the real source of directly available cellulose," p. 130.

Liquid air explosives consist essentially of a combustible compound soaked in liquid air or, better still, in liquid oxygen. The combustible matter must be in a sufficiently fine powder to constitute an adsorbent mass and it is desirable that the grains themselves be porous. When the adsorbing power is so low that the substance will not hold the weight of oxygen necessary for complete combustion, it is necessary to incorporate an inert adsorbent such as diatomaceous earth. A solid adsorbent must be used if the combustible substance is liquid or pasty at the temperature of liquid oxygen, p. 190.

In order to cut down the danger of explosion when grinding the materials for black powder, it is customary to make up two binary mixtures, one of carbon and sulphur, and the other of carbon and potassium nitrate, p. 201. Straight chlorate explosives are too dangerous to make but they are more safe if mixed with a plastic combustible material such as tar, p. 218. The nitrocellulose powders are stabilized with aniline in Italy, with diphenylamine in Russia and Germany, and with amyl alcohol in France.

Wilder D. Bancroft

Die Grundlagen der Dispersoidchemie. *By Andor Fodor. 23 × 16 cm; pp. viii+280 Dresden and Leipzig: Theodor Steinkopff, 1925. Price: 12 marks paper; 14 marks bound.* The author is director of the Institute for Biochemistry and Colloid Chemistry at the Jewish University in Jerusalem and this book is based on lectures that he gave there. The chapters are entitled: the nature of dispersed systems; the action of solutes on dispersion; the formation of dispersed systems; some fundamental laws of dispersoid chemistry; the dispersion processes; the condensation processes; clay as a coarsely dispersed system; proteins as strongly solvated colloids; chemical reactions occurring in colloidal systems, with special reference to fermentation.

This is not a good book. The author has no very definite point of view. He lays great stress on solvation and dehydration as important factors in colloidal equilibrium—which they undoubtedly are—but he is rather hazy as to what they are and how they act. He believes in the existence of three hydrates of sulphuric acid in solution, p. 6, and he accepts Remy's view that sodium ion does not contain over sixty-six molecules of water attached, p. 7. Of the anions in the Hofmenster series he considers that sulphocyanate ion is the least hydrated, p. 42; but he does not explain why potassium iodide should liquefy gelatine more readily than water does. The following paragraph on p. 80 is not very clear even if one makes all sorts of allowances for faulty translation. "We consider solvation before all others as a process which balances the surface energy and it is therefore always correlated with the dispersion process. As we shall explain later in more detail, solvation is quite as important in balancing the surface energy as the other adsorption phenomena." What he probably means is that water often has a strong peptizing action, which nobody can deny.

The author recognizes, p. 11, that a colloidal solution is not a homogeneous phase in the Gibbsian sense because it differs from a salt solution in not being fully defined by the temperature, pressure, and concentration. On the other hand he believes in the experimental continuity of colloidal and true solutions, p. 81.

The author considers the neutralization of an electrical charge on a particle, p 62, as involving a chemical reaction which causes the absolute disappearance of that ion, instead of merely the displacement of the ion or the adsorption of an equivalent amount of an ion having the opposite charge. Consequently he has a terrible time in understanding the very different concentrations at which ions of different valence precipitate arsenious sulphide. The same difficulty comes up in another form with clay, p. 96. Ammonia and sodium hydroxide do not behave exactly alike with clay and yet the author says that they have the same discharge value when in equivalent concentrations. This ignores entirely any effect due to the adsorption of sodium ion.

The author also believes in Wilhelm Ostwald's explanation of rhythmic banding, that it is chiefly a question of supersaturation, p. 245. This cannot be true, in view of the fact that one can get rhythmic banding even when there are some crystals in the clear spaces.

Wilder D. Bancroft

Ueber Wärmeleitung und andere ausgleichende Vorgänge. *By Emil Warburg, 22 × 15 cm; pp. x +106. Berlin: Julius Springer, 1924, Price: $1.40.* The subject is treated under the general heads; conception and properties of equalizing processes; general theory of heat conduction; stationary heat flow; states changing with the time; viscosity. It is rather interesting to notice what apparently different phenomena may be grouped under the same heading, p. 32.

"A substance should become covered with dew if, on a clear night, it is cooled by radiation below the dew-point; but according to Skinner the thin threads of a spider's web do not become covered with dew [because they keep very close to the temperature of the surrounding atmosphere]. The thin threads of the Welsbach mantle keep very close to the temperature of the flame in spite of the radiation. The same thing is true of a very thin platinum wire and consequently one can determine flame temperatures with considerable accuracy by measuring thermoelectrically or radiometrically the temperature of such a platinum wire when in the flame. In a similar way Wood determined the temperature of the glow in a Geissler tube by means of a platinum iridium wire with a diameter of 35μ, making use of the change in resistance." *Wilder D. Bancroft*

Applied Chemistry. *By Ira D. Garard. 19 × 14 cm; pp. vii+496. New York: The Macmillan Company, 1924. Price: $3.25.* In the preface the author says: "The purpose of this book is mainly to provide a text-book for college students who have taken a course in general chemistry and who are further interested in the application of chemistry and the manner in which it functions in modern life. . . . In addition to its use as a text, it is hoped that the book will prove useful to readers who are interested in chemistry because of its relation to their fields in science, art, or industry. . . . The plan of the book aims to systematize so far as possible the practical information of chemistry rather than to merely state the facts."

The book is divided into twenty-two chapters and an appendix which contains fifty-two carefully chosen and interesting laboratory experiments. The chapter headings include: general introduction; solutions; water; the atmosphere; combustion and oxidation; forms of energy and their chemical applications; natural and synthetic organic substances; enzymes and microörganisms; oils, fats, and waxes; carbohydrates: edible proteins; food and nutrition; preparation of foods; colloids; cleansing agents and toilet articles: textiles; dyeing and bleaching; leather and tanning; rubber and plastics; paints, varnishes, and inks; metals and alloys; glass and ceramics; fuels.

The book contains a vast amount of interesting and useful information, clearly and systematically presented. There is no reason why it may not be read with profit by the layman whose knowledge of the chemical principles is limited to the merest fundamentals, for the treatment employed throughout is of the simplest sort.

The reviewer was interested in the author's definition on p. 1 of the term "applied chemistry", which forms the title of the present work. "Applied chemistry need not be so rigidly defined as are most of the other branches. It is more general than industrial chemistry since it is not concerned with manufacturing processes alone. It might be defined as that branch of chemistry which deals with the economic welfare of man." This comes close to being a definition of pandemic chemistry.

The reviewer was particularly interested in the section on dust explosions, and especially in the part on burning aluminum dust, where water and carbon tetrachloride actually encourage the fire (p. 82); also in spontaneous combustion (p. 85) where it is said that the heat generated in a pile of hay is caused by enzyme respiration. The chapter on cleansing agents is good, and the point that soap possesses a strong germicidal action (p. 162) is well brought forward. The table of full values (p. 426) containing the cost per 1000 B.T.U. is especially instructive.

The reviewer, quite naturally, does not agree with the author's point of view in some cases, especially when it is stated that the solution pressure of zinc is its tendency to replace hydrogen ions from solution (p. 91), and that the solution pressure of copper is negative (p. 92). He is also disappointed to find that dyeing with basic dyes is ascribed to chemical union between the dyestuff and the protein fibres, and he does not altogether relish the statement (p. 318) that the theory of direct cotton dyeing is mostly conjecture'

The book fulfils most admirably the purpose for which it was written and the author should be commended for gathering together, in a fairly digestible form, such a fund of every-day chemistry.

T. R. Briggs

PROPERTIES OF AMMONIUM NITRATE

I. A Metastable Inversion in Ammonium Nitrate[1]

BY N. L. BOWEN

Introduction

Ammonium nitrate has long been known to occur in a number of different crystalline forms and its several inversion points have been the subject of much study. Early and Lowry have investigated in a very careful manner all the changes taking place above room temperature and at the ordinary pressure. They found inversions[2] to occur at 32.1°, 84.2°, and 125.2°. Their results confirm earlier work, but the actual values given are the most dependable yet found. The stable transformations of ammonium nitrate are expressed in tabular form in Table I where the designations of these forms are given according to the methods of the crystallographer and the physicist.

TABLE I

Stability ranges of the modifications of ammonium nitrate at atmospheric pressure.

Modification	Range of stability °C
Liquid	169.6 to ——
Isometric (I)	125.2 to 169.6
Tetragonal (II)	84.2 to 125.2
Orthorhombic ? (III)	32.1 to 84.2
Orthorhombic (IV)	−16 to 32.1
Tetragonal (V)	—— to −16

Experimental Method

The writer has recently studied these transformations of ammonium nitrate by a method which permits direct observation of the changes and, at the same time, control and measurement of the temperature. A small quantity of the nitrate, previously dried, is melted on an ordinary microscopic slide and, while liquid, is covered with a cover-slip which is pressed down lightly so that upon cooling one obtains a thin film of the nitrate analogous to the thin section of the mineralogist. This is substantially the method used by Wallerant of preparing slides of nitrate for a similar purpose[3]. In the present study the slide was then placed on a wire support in a small oil bath which was mounted on the stage of a petrographic microscope and which was electrically heated by means of a coil of nichrome wire immersed in the oil.

---

[1] Investigations carried on with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] The properties of ammonium nitrate. Part I. The freezing point and transition-temperatures. J. Chem. Soc., **115**, 1387 (1919).

[3] Sur le polymorphisme et l'isomorphisme des azotes alcalins. Bull. Soc. Min. Fr., **28**, 311 (1905).

The container for the oil was a glass crystallizing dish with flat bottom and the slide could thus be observed by transmitted light as it is ordinarily in the absence of the bath. The temperature was controlled by varying a resistance in series with the nichrome heating coil and was measured by means of a potentiometer and thermoelement of copper-constantan which dipped into the oil and whose junction rested on the mount, being separated from the charge only by the thin cover-slip.

Experimental Results

General observations. With this arrangement it was possible to observe all the stable transformations of ammonium nitrate above room temperature in a very satisfactory manner. The temperatures of the changes correspond with those given by Early and Lowry within the limits of error, especially when the change was in the direction induced by rising temperature. With falling temperature there was often much lag and it was necessary to make the cooling rate very small in order to obtain a value corresponding approximately with that obtained in the reverse direction.

The various forms of ammonium nitrate exhibit sufficient difference of optical properties that they may be distinguished from each other readily as thus viewed under the microscope. The orthorhombic form, stable at ordinary temperature, has refractive indices $\gamma = 1.64-$, $\beta = 1.61$, $\alpha = 1.41+$, and 2V is about 35°. The birefringence is thus extremely high, considerably higher than that of calcite[1].

The orthorhombic (?) or monoclinic form stable between 32° and 84° has a distinctly lower birefringence, though it would still be described as very high. It is further distinguished by an optic axial angle (2V) of nearly 90°.

The tetragonal form stable between 84° and 125° is uniaxial and positive. The birefringence is again distinctly lower, but would still be described as high.

The isometric form is, of course, isotropic.

On account of these differences in optical properties the transformations are readily observed between crossed nicols under the microscope and the various forms identified even when they persist in a temperature region where they are not stable.

The metastable inversion. In addition to, and, in some measure, in place of the stable transformations that have already received so much study, another transformation was observed which was usually more dependable and prompt than the stable transformations. This was the metastable inversion, orthorhombic (IV) $\rightleftharpoons$ tetragonal (II) which occurs at approximately 50°C.

When the molten film of nitrate is cooled it crystallizes, usually with considerable undercooling, to the isometric form which is transformed to the tetragonal form upon further cooling. The actual inversion point may be overstepped as much as 18°. The tetragonal form may then be cooled through the temperature of 84° without showing any change and in practically all cases may be cooled to a temperature somewhat below 50° before the appearance of a new form which is not the orthorhombic ? (III) form stable at this temperature, but the orthorhombic (IV) form stable below 32°. Even with very rapid cooling I have not observed the temperature to fall below 44° without the appearance of the new form, and when the rate of cooling is about one degree per minute the transformation always takes place promptly at 47°-49°. If the orthorhombic (IV) form thus obtained is now reheated, transformation to the tetragonal (II) form takes place at a temperature a little above 50°. Even with a rapid rate of heating I have not observed the orthorhombic (IV) form to persist above 54°, and with a rate of one degree per minute the change takes place promptly at 51°-52.5°. This metastable transformation is thus readily reversible and rather less readily overstepped than the stable transformations when both directions are considered.

---

[1] The index α as given by Thomas and Hallimond at 1.45 (Trans. Faraday Soc., **20**, 5
(1924)) is much too high, indeed the match with amyl valerate of index 1.411 is sensibl
perfect.

One may sometimes heat the nitrate back and forth through the inversion point a score or more of times with repeated inversions in both directions and thus retain the one or the other of the forms in its metastable region for a total of several hours without the appearance of the stable, orthorhombic ? (III) form. If the temperature is carried below 32° no change occurs at that point, since the nitrate is already in the orthorhombic form stable below that temperature, and likewise if it is carried above 84° no change occurs at that point, since it is already in the form stable above that temperature. Moreover, when the temperature is thus carried upward or downward into the regions of stable existence of the respective forms no change is apparent in the tendency of these forms to persist in the metastable region and to exhibit the metastable inversion at 50° when the temperature is brought back to that value.

Eventually, however, any given charge of nitrate appears to change its mind and decide to assume the stable modification. I have observed this to take place in only one way and that immediately after the metastable transformation in the cooling direction. The tetragonal form is observed to change to the orthorhombic in the usual way and then immediately the stable orthorhombic ? (III) form puts in an appearance. It starts at one or two centers from which it spreads with a circular front and ordinarily begins to form before the metastable transformation is complete in all parts of the charge, so that the two changes can frequently be seen passing across the field of the microscope at the same time, the metastable inversion somewhat in advance of the change to the stable form. It thus affords an excellent example of Ostwald's law of successive reactions.

If the charge is now cooled below 32°, transformation to the orthorhombic (IV) form occurs at that temperature, and if it is heated above 84°, inversion to the tetragonal (II) form occurs, but the metastable transformation at 50° is now no longer obtained. By carrying the charge above 125° and thus changing it into the isometric (I) form the metastable inversion can frequently be induced to reappear when the charge is again cooled and by remelting the charge its reappearance is practically assured.

Earlier Work indicating the Existence of the Metastable Inversion

Certain aspects of the observations here recorded have been noted by others. Thus Early and Lowry note that undercooling readily occurs at the 84° inversion point and state that "in many cases the salt was cooled to 32° without any indication that this change of crystalline form had taken place".[1] While there is nothing inherently improbable in such a degree of undercooling, it was never observed in the present work, the metastable transformation always occurring at a temperature well above 32°.

Wallerant noted that ammonium nitrate could be cooled through the 84° inversion point without inversion and that the tetragonal (II) form might change directly to the orthorhombic (IV) form[2]. He did not, however, note that the change took place at any particular temperature. Behn, studying the inversions dilatometrically, noted that the tetragonal modification could easily be cooled to a temperature of 45°, and definitely suggested that this temperature was determined by the II-IV inversion, though the final result was always the form III. He calls attention to the fact that Tammann had studied the II-IV inversion at high pressures, where it becomes a stable inversion, and that extrapolation of his curve to atmospheric pressure would indicate an inversion point of 45°.[3]

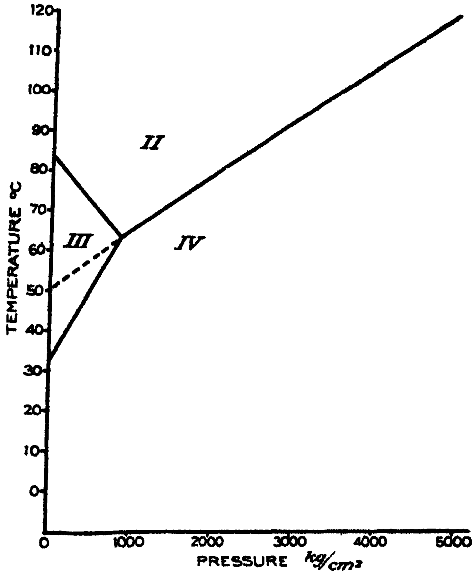


FIG. 1

Curve of variation of the orthorhombic (IV) $\rightleftarrows$ tetragonal (II) inversion of ammonium nitrate (after Bridgman) showing its metastable extension (broken curve) and indicating an inversion point of 50.5° at atmospheric pressure.

---

[1] Op. cit., p. 1392.

[2] Op. cit., p. 319.

[3] Proc. Roy. Soc., 80, 449 (1908).

There have thus been a number of indications of the existence of this transformation with falling temperature, but it has not been observed that it was definitely reversible and could be obtained with rising temperature as well.

Concerning the actual temperature of the inversion it is to be noted that the temperature of 45° where inversion was noted by Behn is definitely too low. While with rapid cooling it may fall to that temperature, with slower cooling it takes place at a temperature of from 47°-49° and with slow heating it occurs at 51°-52.5°. Having regard for the fact that all the inversions of ammonium nitrate are more easily overstepped in the cooling direction than in the opposite direction, we may place the inversion point at 50° with the suggestion that it is a little higher rather than lower, but the accuracy of the determinations does not warrant any more definite figure.

If we turn to Bridgman's determinations of the transformations of ammonium nitrate under pressure we find that he has studied the II-IV transformation throughout its stable range of some 8000 atmospheres[1]. A relatively short extrapolation of his values into the metastable region at low pressures indicates a value of 50.5° for the transformation at atmospheric pressure. This value is in good agreement with that observed in the present study. Bridgman's results on ammonium nitrate are here reproduced in Fig. 1, with the metastable extension of the II-IV curve added. Perhaps the temperature 50.5°, as determined by extrapolation from Bridgman's results, would be a more satisfactory value for recording as a constant of ammonium nitrate than any that could be determined directly in the metastable region.

Summary

Besides the several well-known transformations of crystalline ammonium nitrate it is found that a reversible transformation takes place at approximately 50°C. The method of studying the inversion is that of direct observation under the petrographic microscope by which means the various forms can be identified in virtue of differences of optical properties. The inversion at 50°C is found to correspond with the change, orthorhombic (IV) $\rightleftharpoons$ tetragonal (II). At this temperature both forms are metastable, nevertheless the transformation is, in many respects, more prompt and dependable than most of the stable inversions. Extrapolation of Bridgman's values for the II $\rightleftharpoons$ IV inversion at high pressures, where it is a stable transformation, indicates a value of 50.5° for the temperature of this change at atmospheric pressure. This temperature is in good agreement with that here directly determined.

---

[1] P. W. Bridgman: "Polymorphic Changes under Pressure of the Univalent Nitrates". Proc. Am. Acad. Arts Sci., **51**, 605 (1916).

PROPERTIES OF AMMONIUM NITRATE

II. The System: Ammonium Nitrate-Ammonium Chloride[1]

BY N. L. BOWEN

Introduction

There has recently appeared a series of papers on the properties of ammonium nitrate, the result of investigations instituted by Professor Lowry but carried on latterly by Professor Perman. One of these has already been referred to in Part I of the present series. Another deals with the reciprocal salt-pair, ammonium nitrate and sodium chloride[2]. The binary system: NH_4NO_3-NH_4Cl is included within this salt-pair system and was accordingly investigated by Perman. He concludes that "no isomorphous mixtures or double salts are formed".[3] The present investigation confirms his conclusion regarding double salts but shows that with respect to isomorphous mixtures his conclusion is subject to revision.

The ordinary method of investigating such a system is to subject mixtures to thermal analysis in the form of heating or cooling curves. When the results from a number of mixtures are assembled it is frequently possible to deduce a complete equilibrium diagram, but not infrequently there may still be some ambiguity. The present investigation arose from the fact that a marked break was obtained at 109°C on the heating curve of a mixture of ammonium nitrate with 3 per cent ammonium chloride. Since no break was obtained at 125° it was considered probable that the break was due to the tetragonal (II) ⟶ isometric (I) inversion of the nitrate as changed by the presence of NH_4Cl, a fact which necessitates solid solution. It was felt, however, that multiplication of heating curves would probably still leave ambiguity and that a method of direct observation of the changes should be adopted.

Accordingly various mixtures were studied in an oil bath under the microscope, the arrangement of which has already been described in Part I. Thus was permitted, at measured temperatures, the direct observation of inversions, formation and unmixing of solid solutions, beginning of melting and completion of melting, in fact all the changes necessary for the construction of a complete equilibrium diagram. For the study of those changes that may take place slowly such as the mixing and unmixing of solid solutions, it was possible to keep the temperature of the oil bath constant within about one degree for several hours by using a storage battery as a source of current.

The investigation as a whole constitutes an excellent example of one manner in which the petrographic microscope may be used as an aid to the study of chemical equilibrium. On account of the fact that all of the changes involved can be viewed actually in progress, the question of alternative interpretations scarcely enters. This is not always true in equilibrium diagrams, especially of systems where solid solution occurs, as evidence of which fact might be cited the several forms of the iron-carbon diagram that are current. The range of variety of the phenomena exhibited and directly observable the relative ease of attainment of equilibrium, the accessibility of the temperatures involved and the consequent simplicity of apparatus required render the present system a very advantageous one to assign to students for practice purposes. They would thus be put in the way of acquiring a practical acquaintance with the principles of phase equilibrium and also of gaining some familiarity with the manipulation of the polarizing microscope.

---

[1] Investigations carried on with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] E. P. Perman: J. Chem. Soc., **121**, 2473 (1922).

[3] Op. cit., p. 2480.

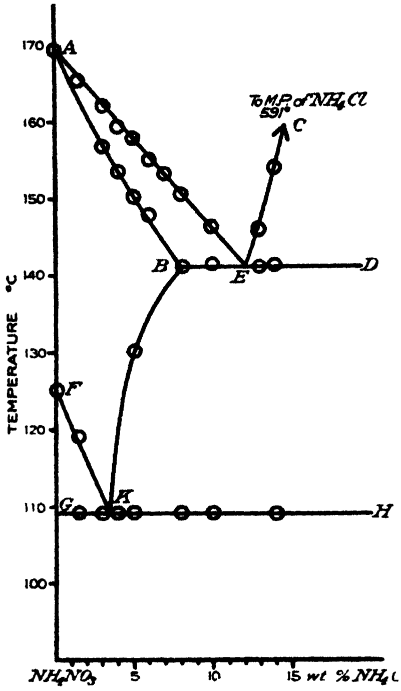


Fig. 1

Equilibrium diagram of the system: ammonium nitrate-ammonium chloride.

ABKF —Isometric mix-crystals

AEB —Isometric mix-crystals and liquid

GKF —Isometric mix-crystals and tetragonal NH_4NO_3

DBKH —Isometric mix-crystals and isometric NH_4Cl

CED —Liquid and isometric NH_4Cl

Below *GKH* —Tetragonal NH_4NO_3 and isometric NH_4Cl.

Preparation of Mixtures

The materials used in the preparation of mixtures were J. T. Baker's analyzed ammonium nitrate and ammonium chloride. These were powdered and dried in an evacuated desiccator over P_2O_5 after the method recommended by Early and Lowry[1]. Weighed amounts were then mixed in various proportions and the mixture fused in a short test tube by immersing it in an oil bath to avoid excessive heating. The mixture was well stirred while liquid and then chilled rapidly to prevent segregation. About 2 g. of each mixture to be investigated was thus made; the fused cake obtained was powdered and kept in the vacuum desiccator until needed for study.

---

[1] J. Chem. Soc., **115**, 1389 (1919).

For the investigation of each mixture a small amount of the powder was placed on a specimen glass, heated gently until melted, covered with a cover slip and placed in the oil bath on the stage of the microscope. For most of the observations a magnification of 80 diameters was used, but for the study of some of the finer structures such as those produced by unmixing of solid solutions resort was had to some 200 diameters. By working in this manner and noting not only the temperature at which changes occurred but also the nature of the changes the results given in Table I were obtained. It was found that many of the changes were readily overstepped in the cooling direction but were prompt in the opposite direction. In the case of the solidus and liquidus, especially, it is essential that these be determined in the heating direction.

TABLE I

Temperatures of observed changes in NH_4NO_3-NH_4Cl mixtures

Composition Per cent NH_4Cl	Tetragonal→Isometric inversion °C	Beginning of melting °C	Completion of melting °C
0	125.5	169+	
1.5	109 (in part)	——	165.5
3.0	109 (in part)	157	162
4.0	109	153+	159.5
5.0	109	151	158
6.0	109	148	155
7.0	109	——	153
8.0	109	141	150.5
10.0	109	141.5	146.5
13.0	109	141	146
14.0	109	141.5	154

These results, together with a few others that do not lend themselves to tabulation, are expressed in diagrammatic form in Fig. 1.

Correspondence of the Results with those of Perman

The diagram obtained by Perman is reproduced in Fig. 2 and comparison shows that the liquids of ammonium nitrate and the composition and temperature of the eutectic are in complete agreement with my results. The upper points on the NH_4Cl liquidus are somewhat lower than those determined by Perman but these are very difficult of determination because some decomposition sets in and a little gas is evolved so that the error here may be perhaps four or five degrees. It is sufficient to know that the NH_4Cl liquidus rises steeply from the eutectic.

It is especially to be noted that some features of Perman's results themselves point directly to the existence of solid solution. Thus he obtained a remarkable eutectic arrest in the 11 per cent mixture, the temperature remaining constant for fully seven minutes. On the other hand he obtained no break whatever in the six per cent mixture at that temperature, though in the absence of solid solution the pause should be about half as long[1]. The absence of the arrest is, of course, due to the fact that the six per cent mixture lies within the limits of solid solution.

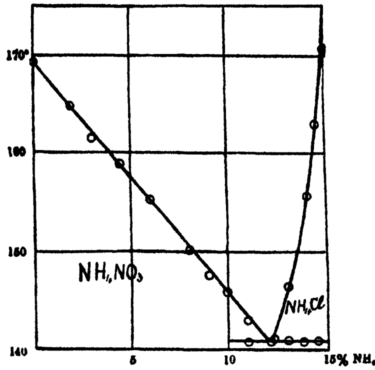


FIG. 2

The system: ammonium nitrate-ammonium chloride (after Perman).

Moreover, in his later work, in which he separated the crystals from liquid by a method of filter-pressing and then analyzed the crystals, he was unable to get the NH_4NO_3 crystals nearly as pure as the NH_4Cl crystals obtained on the other side of the eutectic[2].

The significant difference between the two diagrams is that the new one shows the liquidus of ammonium nitrate to be that of ammonium nitrate mix-crystals and not of the pure salt. The existence of these mix-crystals brings in the phenomena of melting intervals, inversion intervals and unmixing of solid solutions which are the really interesting features of the diagram. The existence of such features in mix-crystals or solid solutions is, of course, well known, but the phenomena resulting have seldom been observed actually in progress with the clarity exhibited in the present system, so that some description of the observations would appear to be called for.

Melting and Crystallization of the Solid Solutions

Both the beginning and completion of melting of the solid solutions can be observed very definitely. Melting begins with the formation of narrow channels of liquid all through the originally homogeneous[3] solid. As the temperature is slowly raised these gradually widen at the expense of the intervening areas of solid until they finally occupy the whole field and the solid has completely disappeared.

Crystallization is practically the reverse of this. Upon cooling there is ordinarily five degrees or more of undercooling and then crystallization appears, not at numerous dispersed points, but at one, or at most, two or three points from which branching crystal forms spread all through the liquid. As the temperature falls this skeleton grows at the expense of the intervening areas of liquid until finally all of the liquid is exhausted.

---

[1] Perman: op. cit., p. 2474. Fig. 1.

[2] Perman and Dawkins: J. Chem. Soc., **125**, 1241-2 (1924).

[3] "Homogeneous" is here used to designate the presence of only one phase and not to indicate uniformity of crystallographic orientation. When the latter condition is referred to it is specifically so designated.

It can sometimes be definitely observed that, as may be deduced from the diagram, the solid solution first separating is of different composition from that later formed. The index of refraction of ammonium nitrate mix-crystals increases as the content of NH_4Cl increases. The branching crystals first formed are relatively poor in NH_4Cl and therefore of relatively low refractive index, and when crystallization is complete the original skeleton is still distinguishable from the rest of the otherwise homogeneous mass by a lower refractive index, detected by the half-shade method familiar to petrographers. There are, of course, no sharp boundaries, but a general fading of the one into the other.

As a result of such zoning of crystals the crystallization interval obtained on cooling is greater than the true equilibrium interval, for such zoning represents a failure of true equilibrium. It should be noted, too, that, for the determination of the melting interval (rising temperature), material which has been crystallized in such a way as to give zoning can not be used because it will give too low a temperature of beginning of melting. Perfectly homogeneous solid solutions for the study of the melting interval were prepared by making the amount in the usual way and dropping it quickly into the oil bath, which was already at a temperature of 130°. The preparation is thus chilled instantly to 130° and crystallizes to a homogeneous solid solution.

Melting and Crystallization of Eutectiferous Mixtures

Eutectiferous mixtures such as that containing 10 per cent NH_4Cl are best crystallized in a similar manner. They then consist of areas of homogeneous mix-crystal with interstitial patches of a fine-grained intergrowth of NH_4Cl and nitrate mix-crystals. When this is heated the fine-grained intergrowth is seen to melt as a whole at 141° and then with rising temperature the excess crystals dissolve in the liquid. One thus obtains direct visual evidence that the change occurring at 141° is the melting of the eutectic intergrowth.

If crystallized relatively slowly by cooling in the oil bath, so that zoning of mix-crystals occurs, even mixtures that lie within the limits of solid solution may show some residual eutectic intergrowth. Thus the seven per cent mixture, though it can readily be shown, when properly crystallized, to be within the solid solution area, may at times show some eutectic. This is due to the fact that the first crystals formed have only about 4 per cent NH_4Cl and unless these can, with falling temperature, be completely made over into crystals richer in NH_4Cl by reaction with the liquid, the final liquid must have considerably more NH_4Cl than 7 per cent, that is, must lie within the eutectiferous region.

Thus the 7 per cent mixture may or may not develop some eutectic mixture, depending on the conditions of crystallization. In other words free NH_4Cl as a separate crystalline phase may or may not develop, depending on the opportunity for reaction (interchange of material) between crystals and liquid during crystallization. This factor is so important in silicate systems where solid solution is so prevalent that I have sought to emphasize it by giving it a name for which I have suggested the "reaction principle".[1] In mineral systems, as in the present system, the working of the reaction principle permits the development or the non-development of certain compounds as separate crystalline phases depending on the conditions of crystallization. Desch has offered objection to the principle and refers to it as "abandonment of the equilibrium diagram" though he fails to point out just where the deviation comes in[2]. It is, as a matter of fact, a direct deduction from equilibrium diagrams and is by no means confined to silicates. Here we have direct visual evidence of its working in a salt system and one could cite many systems involving either solid solution or incongruent melting and coming from Desch's own field of metallurgy where the working of the reaction principle is of paramount importance in determining the phases present in an alloy and therefore in determining the properties of the alloy.

Limit of Solid Solution

By crystallizing rapidly at 130° in the manner described it can readily be observed that most of the mixtures in the solid solution area form a single homogeneous crystalline phase. In the 8 per cent mixture such a phase forms first at 130° but, immediately, separation of NH_4Cl occurs as skeletons of cubic pattern throughout the mass. Though both the nitrate mix-crystals and the NH_4Cl are isotropic, the presence of two substances and the identity of each is readily established on account of the much higher refractive index of the NH_4Cl. If, now, the temperature of the mass is raised to 138°, a temperature only a little below the eutectic, the NH_4Cl is observed to decrease in amount slowly. After 1½ hours at that temperature there is only a bare trace left and it persists with further heating at this temperature. If the temperature could be held exactly at the eutectic without passing a little above it, and thus inducing melting, it is probable that this last trace of NH_4Cl would disappear. At any rate the amount left at 138° is so small that the extent of solid solution may be said to be nearly if not quite 8 per cent.

Metastable Solid Solutions

Even mixtures well beyond the limit of solid solution, indeed on the NH_4Cl side of the eutectic, may crystallize in such a way as to give transitory, metastable, solid solutions. Thus the mixture with 13 per cent NH_4Cl will cool in the oil bath to about 136° (well below the eutectic) before crystals form and it then crystallizes to a single, homogeneous phase. This phase is scarcely formed, however, when it begins to separate into two phases. This unmixing starts at one or two centers from which it spreads after the manner of an inversion. It is plainly the unmixing of a homogenous phase and not the gradual coarsening of a sub-microscopic intergrowth of two phases, for this latter would take place very gradually and all parts of the mass would, at any time, be at the same stage of coarsening. Contrary to this, the actual change at any point is an instantaneous one from a perfectly clear, homogeneous mass to a turbid intergrowth of two phases which does not thereafter change any further. The change is propagated from point to point as a circular wave which may take two, three or even five minutes to traverse one centimeter. At the end of this 5 minutes the portion not yet reached by the wave of unmixing is still the clear, homogeneous solid solution that it was originally. While there may thus elapse several minutes between the time of formation of the metastable solution and the *completion* of unmixing in all parts of the mass, I have never observed any appreciable interval between the formation of the homogeneous crystalline phase and the *beginning* of unmixing at some point in the mass. It is not suggested that this is a necessary property of metastable solid solutions. It is merely pointed out as a fact in the present instance.

---

[1] N. L. Bowen: "The Reaction Principle in Petrogenesis". J. Geol., 30, 177-198 (1922).

[2] C. H. Desch: Trans. Faraday Society, 20, 472-3 (1925); and also Presidential Address Section B, Chemistry, British A. A. S., Southampton, 1925, p. 20.

Mixing and Unmixing of Solid Solutions

Reference has already been made to the unmixing of solid solutions especially in connection with the metastable solid solutions and also to both mixing and unmixing in describing the determination of the limits of solid solution on the 8 per cent mixture. The phenomena observed on crossing the unmixing curve *BK* in any of the mixtures between 3 1/2 per cent (*K*) and 8 per cent (*B*) are in most respects the same as those already described for the 8 per cent mixture. Thus the 5 per cent mixture, when crystallized rapidly at 142°, gives a single homogeneous mix-crystal phase and it remains indefinitely as such if the temperature is maintained at that value. If, however, the temperature is lowered to 115°, unmixing occurs in the form of the separation of a skeleton of NH_4Cl of cubic pattern. This separation is somewhat different from that occurring in the metastable solid solutions. It takes place gradually and uniformly in all parts of the mount, appearing first as a slight turbidity which increases until finally definite, though minute, stripes of higher refractive index (NH_4Cl) are to be made out. If the homogeneous mass is now slowly reheated (in the actual example the heating rate was 10° per hour) the NH_4Cl can be seen to decrease in amount. At 130° it has finally disappeared and the preparation is again a single homogeneous phase. It was also ascertained that at 125° some NH_4Cl persists after two hours and without apparent diminution in amount after the first few minutes. It was taken, therefore, that disappearance at 130° represents equilibrium at the point on the curve *BK* at 5 per cent NH_4Cl was accordingly placed at that temperature.

Inversion and the Inversion Intervals of the Solid Solutions

When a mount of pure NH_4NO_3 is slowly heated the inversion from the birefracting tetragonal form to the isotropic form is observed to take place at 125.5°. In all mixtures containing NH_4Cl (none with less than 1.5 per cent was examined) the same change takes place at 109° (*GKH*). Below that temperature all mixtures are definitely inhomogeneous, both tetragonal NH_4NO_3 and cubic NH_4Cl being recognizable. This is true even of the mixture containing only 1.5 per cent NH_4Cl so that from direct observation we know that there is little if any solid solution of NH_4Cl in the tetragonal modification of NH_4NO_3. Immediately above 109° the condition of the mixture depends upon whether it is of a composition lying to the right or to the left of *K*. Those compositions to the right of *K* (richer in NH_4Cl) consist of isotropic mix-crystals and excess NH_4Cl as such. Those to the left of *K* consist of isotropic mix-crystals and excess birefracting (tetragonal) NH_4NO_3. Indeed it was on this basis that the composition of the point *K* was established. The 4 per cent mixture was found to belong to the one class and the 3 per cent to the other. The point *K* was believed to be thus located with sufficient accuracy and was placed midway or at 3.5 per cent.

It may be of interest to note that if we calculate the concentration of the solid solution which should have an inversion point of 109° by means of the approximate formula $\triangle T = \frac{RT^2}{L} \cdot \frac{N}{N_0}$ we obtain a value of approximately 3.4 weight per cent NH_4Cl which is in agreement with the experimental finding that it is between three and four per cent. In the formula $\triangle T$ is the difference between the temperature of any phase-change (melting, boiling or inversion) of a pure solvent and that of the same change in a solution containing N mols of solute to N_0 mols of solvent. T is the temperature of the phase-change in the pure solvent, L the latent heat of the phase-change per mol and R, the gas constant. In the present case the temperature of the inversion of the pure nitrate is 125°C whence $T = 398°$ and $\triangle T = 16°$. The latent heat of inversion per gram $= 13.0$ calories[1], whence $L = 1040$ calories.

The further behavior, with temperature rising above 109°, of mixtures to the right of *K* (those with excess NH_4Cl) has already been described. Those to the left of *K* remain to be discussed. They contain in addition to isotropic mix-crystals an excess of tetragonal NH_4NO_3. The latter is very conspicuous under crossed nicols, for it occurs as bright birefracting filaments ramifying through the dark, isotropic ground mass. When the temperature is slowly raised these filaments gradually narrow as a result of the absorption of their substance into the surrounding isotropic phase. Thus, if the 1.5 per cent mixture is held at 118° for 35 minutes there is at first marked absorption of the filaments, but the change finally comes to rest with minute filaments still persisting. On the other hand, at 120° disappearance of the filaments is complete in 20 minutes. On the basis of these determinations the point on the curve *FK* corresponding to the 1.5 per cent mixture was placed at 119°.

Under conditions of relatively rapid heating, these filaments of tetragonal NH_4NO_3 behave in a different manner. There is then insufficient opportunity for diffusion into the adjacent phase and they act as they would in its absence. The temperature may accordingly be raised to 125.5° where they promptly invert to the isotropic form. We have thus additional proof that these filaments are pure, tetragonal NH_4NO_3 and that this form of NH_4NO_3 takes no NH_4Cl into solid solution. Even after inversion of the filaments to the isotropic form, whereby they have become the same phase as their surroundings, they are, nevertheless, a different concentration of that phase and are still distinguishable by virtue of a lower refractive index. This difference gradually fades out, however, and in a few minutes no observable difference persists.

---

[1] This value was calculated by Bridgman from the results of his study of the effect of pressure on the transition point. Proc. Am. Acad. Arts Sci., **51**, 614 (1916).

The freedom of diffusion in these solids, which is evidenced by this and other phenomena already described, is very remarkable when it is considered that the temperatures concerned are but little above the boiling point of water.

The inversion of the solid solutions (*G-K*) with falling temperature should take place when the curve *FK* is crossed but as a matter of fact undercooling ordinarily occurs. Filaments of birefracting, tetragonal NH_4NO_3 can be developed, however, in a mass that was originally a homogeneous isotropic solid solution by cooling it into the region *FKG* and holding it there.

It should be pointed out that some mixtures can be crystallized in such a way as to give both the effect characteristic of mixtures to the left of *K* and that characteristic of mixtures to the right of *K*. This is accomplished by the relatively slow crystallization induced by cooling the oil bath with the mount in place and was observed to occur in the 4 per cent mixture. As has already been stated, the crystallization begins with the separation of a framework with less than 4 per cent NH_4Cl which is later filled in by material with more than 4 per cent NH_4Cl and the difference is apparent in the lower refractive index of the original framework. Further cooling of a mass so constituted and holding it at a temperature of 113° induce separation of birefracting NH_4NO_3 in the parts corresponding with the original framework and of a cubic skeleton of NH_4Cl in the other parts.

Lack of Solid Solution in the other Modifications of Ammonium Nitrate

We have already noted the evidence that there is no solid solution of NH_4Cl in the tetragonal form of NH_4NO_3. A study of the other inversions of the nitrate, that at 84°, that at 32°, and the metastable inversion at 50°, shows that there is no appreciable change in any of them in the presence of NH_4Cl. From this fact it may be deduced that, like the tetragonal form, none of the other low-temperature forms of ammonium nitrate takes ammonium chloride into solid solution. Therefore for the complete diagram of stable equilibrium above room temperature Fig. 1 requires to have added to it only two horizontal lines, one at 84° and one at 32°.

Summary

A re-examination of the system ammonium nitrate-ammonium chloride gives results that agree with those of Perman as to the position of the liquidus curves and the eutectic but reveals a series of solid solutions not found by him. The method of investigation is that of direct observation under the microscope whereby the various crystalline phases can be identified by means of their optical properties and phase-changes can be observed actually in progress.

It is thus found that all mixtures from pure NH_4NO_3 as far as eight per cent NH_4Cl crystallize to a homogeneous. mix-crystal phase of isometric

symmetry. In consequence of the existence of this mix-crystal or solid solution series the phenomenon of the eutectic does not enter until after the limits of solid solution are passed, each member of the series beginning to melt at a successively higher temperature as pure NH_4NO_3 is approached.

In addition to these melting intervals of the solid solutions their inversion intervals can likewise be observed directly. The isometric (I) ⟶ tetragonal (II) inversion changes from 125.5° for pure NH_4NO_3 to 109° for the solid solution containing 3.5 per cent NH_4Cl. At 109° the curve of unmixing of solid solutions is encountered and along this curve the phenomena of mixing and unmixing of solid solutions take place and can be directly observed. Thus even changes involving diffusion in the solid state take place with comparative readiness in these materials.

All of the facts are embodied in the equilibrium diagram, Fig. 1.

PROPERTIES OF AMMONIUM NITRATE

III. A Note on the System: Ammonium Nitrate-Ammonium Sulphate[1]

BY N. L. BOWEN

Perman, continuing his studies of NH_4NO_3, has published in collaboration with Howells the results of an investigation of the system NH_4NO_3-$(NH_4)_2SO_4$ by the method of thermal analysis. They found that the melting point of NH_4NO_3 rises with addition of $(NH_4)_2SO_4$ and concluded therefore that there was formation of solid solutions[2].

Freeth, while recognizing this as a possible interpretation of the thermal results, offers the alternative suggestion that we have here an example of the limiting case of the eutectic. The eutectic is assumed to lie sensibly at the composition of the component NH_4NO_3 and therefore, of course, sensibly at the temperature of melting of NH_4NO_3 and the rising curve is assumed to be the liquidus of the double salt, $3NH_4NO_3 . (NH_4)_2SO_4$.[3] Freeth offers this system by way of an example of one in which a little more work would clear up moot points and suggests the determination of an isotherm at 170°C with water. This would almost certainly offer more than a little work and not improbably would still permit alternative interpretation. There is a simpler and more direct method, namely, that of actual observation of the phases and phase-changes under the petrographic microscope, and the present note gives the results of applying this method to decide the point at issue.

The method is that already described in former papers of the present series and consists in preparing a microscope mount of the mixture by melting it on a specimen glass, covering it with a cover slip and then observing the various phase-changes in an oil bath of controlled and measured temperature mounted on the stage of a polarizing microscope.

No attempt was made to work out the complete system: Only enough work was done to decide whether the rising liquidus was that of NH_4NO_3 mix-crystals or the 3:1 double salt, which required the preparation of only one mixture. The mixture made was that containing four per cent $(NH_4)_2SO_4$.

When this mixture is melted and allowed to cool in the oil bath it is seen to crystallize to a single, homogeneous, isotropic, mix-crystal phase or solid solution. The refractive indices of the 3:1 double salt have been determined by Thomas and Hallimond[4] to be $\gamma = 1.536$ and $\alpha = 1.521$. A small fraction of one per cent of such material, present in addition to isotropic NH_4NO_3, could not escape detection under the microscope. There is the possibility, of course, that the double salt has a higher-temperature, crystalline form which is isotropic, but even if this form were present as such it would require to have almost exactly the same refractive index as NH_4NO_3 to escape detection. The possibility of such extreme correspondence is very remote and in any case the fact that the sulphate exists in solid solution is proven by other observations now to be given.

---

[1] Investigations carried out with the co-operation of Peerless Explosives Company, to whom we take this opportunity of expressing our thanks.

[2] Perman and Howells: J. Chem. Soc., **123**, 2130 (1923).

[3] F. A. Freeth: J. Phys. Chem. **29**, 506 (1925).

[4] "Chemical and physical properties of Oppau ammonium sulphate-nitrate". Trans. Faraday Soc., **20**, 57 (1924).

When the preparation is further cooled no change of any kind is observed until a temperature of about 100°C is reached, when inversion to a birefracting mass occurs. The preparation is now plainly inhomogeneous, i.e., is made up of two different crystalline phases, the one definitely recognizable as tetragonal NH_4NO_3, the other too small in amount to permit definite determination of its properties. The exact temperature at which the inversion takes place with falling temperature is of no particular significance for undercooling readily occurs, but, upon slow reheating, the mass is observed to revert to the isotropic state at 118.5°C, a full 7° below the corresponding inversion in pure NH_4NO_3. Such a change of inversion point can be brought about only as a result of solid solution. Moreover, the direction of the change—a lowering—is such as to prove the greater solid solubility of the $(NH_4)_2SO_4$ in the higher temperature (isotropic) form of NH_4NO_3 than in the lower temperature (tetragonal) form[1].

The preparation is now again a single, homogeneous, isotropic, mix-crystal phase which has been produced in this case from two solids so that the possibility can be immediately rejected that the similar phase produced by cooling the liquid was a metastable phase that failed to unmix.

All of the facts are therefore in complete accord with the conclusion of Perman and Howells that solid solutions are formed and their rising liquidus is properly interpreted as the result of this fact. The present work proves directly only that the solid solution extends at least as far as 4 per cent, but the smooth rise of the liquidus as far as 8 per cent indicates that it is all the one liquidus and that solid solution extends beyond that point, for the solidus must, of course, lie at least a little on the sulphate side of the liquidus.

Further work would be necessary to determine the limiting concentration of this mix-crystal series, but there is nothing in the existence of such a series that is inconsistent with the proved existence of the 3:1 double salt at 70° or, indeed, with its stability in contact with liquid at higher temperatures.

Summary

By the method of direct observation of phase-changes under the microscope it is proved that the rising liquidus in the system, NH_4NO_3-$(NH_4)_2SO_4$ is caused by solid solution, as Perman and Howells conclude, and not by the limiting position of the eutectic, a possible alternative suggested by Freeth.

Geophysical Laboratory,
Carnegie Institution of Washington,
January, 1926.

---

[1] It was observed that the metastable inversion which takes place at 50° in pure NH_4NO_3 took place at sensibly the same temperature in the present mixture, from which fact it may be inferred that neither the tetragonal nor the orthorhombic form of NH_4NO_3 takes sulphate into solid solution at least at that temperature.

THE EFFECT OF TEMPERATURE UPON THE GROWTH OF YEAST IN VARIOUS MEDIA

BY F. F. SHERWOOD AND E. I. FULMER*

Introduction

In previous communications from this laboratory[1] it has been shown that the rate of growth of yeast depends not only upon the kinds of nutrients present but also upon their concentrations. In the case of ammonium salts there are optimum concentrations which shift with temperature, a higher concentration being required for optimum results with rise in temperature. This is true not only in a synthetic medium but holds likewise for beer wort. The optimum concentrations of ammonium salt for the growth of yeast in the medium at any temperature is that concentration in which a protein, wheat gluten, is least swollen. The generalization was made[2] that "if the addition of ammonium salt to a medium increases its ability to dehydrate wheat gluten, the addition will likewise improve the medium for the growth of yeast, the effect being a maximum in any combination in which the gluten is least swollen".

It was likewise pointed out in a preliminary communication on the subject[3] that since there are at least two optimal concentrations of ammonium salt for the growth of yeast at a given temperature it follows that for a given concentration of the salt there are at least two optimal temperatures. In Table I are given the values of the optimum temperatures for several standard media for yeast growth.

TABLE I

Calculated Optimum Temperatures for Several Standard Media for the Growth of Yeast

Investigator	Ammonium salt	Normality	Optimum Temperatures	
Pasteur	tartrate	0.00109	− 29.5	−26.0
Nägeli	tartrate	0.00435	− 23.8	−25.4
Mayer	nitrate	0.00936	− 15.0	−24.2
Amand	chloride	0.0187	+ 1.4	−21.9
Raulin	nitrate and sulfate	0.0359	+ 31.6	−17.9
MacDonald	sulfate	0.0454	+ 48.2	−15.5
Laurent	sulfate	0.0713	+ 93.7	− 9.5
Cohn	tartrate	0.109	+159.	− 0.47

---

* From the Laboratory of Biophysical Chemistry, Chemistry Department, Ames.

[1] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc., 43, 191 (1921); Ind. Eng. Chem., 16, 921 (1924); Fulmer: "Colloid Symposium Monograph", 2, 204 (1924).

[2] Fulmer, Sherwood and Nelson: Ind. Eng. Chem., 16, 921 (1924).

[3] Fulmer: "Colloid Symposium Monograph", 2, 204 (1924).

In only one instance, that of Raulin's medium, is an optimum temperature within the viable range. A rise in temperature in a medium with a given concentration of ammonium salt is equivalent in the effect upon the growth of yeast to the lowering of the concentration of the salt at a given temperature. Evidently the term "optimum temperature" for the growth of an organism has no general meaning but is a function of the kinds of materials present and of their concentrations.

Data obtained regarding the effect of temperature upon the growth of an organism in a medium of constant composition are the resultant of two factors, the effect of temperature per se and its effect upon the physical chemical environment. This may be illustrated as follows. If the growth of yeast in Amand's medium be studied between 10° and 30° the growth rate will be increased by rise in temperature but also retarded due to the increasing "distance" from the optimum of +1.4°; with MacDonald's medium the growth rate will be accelerated by the increase in temperature and likewise by that fact of the approach to an optimum of +48.2°; with a medium such as that of Cohn the effect will be complex for with rise in temperature the growth rate will be accelerated by the increase in temperature but retarded as the temperature goes away from the medium of −1.7° and accelerated as the optimum of +159 is approached.

It would seem then that the effect of temperature per se upon the growth of yeast in a medium of a given composition can be determined only on the basis of growth rates in the medium with the optimum concentrations of the components for each temperature. Data are here presented on the growth of yeast at various temperatures in media whose composition is adjusted to optimum conditions and the results compared to those obtained in media not so adjusted as well as with data obtained by other investigators.

The yeast used had been growing continuously in a synthetic medium for five years and came originally from a cake of Fleischmann's yeast and is identical with the yeast described previously[1] as No. 11. The number of cells in each case was determined by means of the Thoma-Zeiss counting chamber and is indicated as "count". The "count" is the number of cells in sixteen small squares so that when the count is one there are 250,000 cells per cubic centimeter. In every case the flasks were inoculated so that the initial count was one, the inoculation being made from an actively growing culture in order to reduce any "lag phase" to a minimum.

In the determination of the growth rates the flasks were gently rocked after the method described by Clark[2] and for reasons discussed by him.

The beer wort was made by mashing, at 55°, 360 grams of distiller's malt with 1150 cc. of distilled water for 24 hours. The mixture was filtered through towelling, then through filter paper and heated for thirty minutes under 15

---

[1] Fulmer and Christensen: J. Phys. Chem., **29**, 1415 (1925).

[2] Clark: J. Phys. Chem., **26**, 42 (1922).

TABLE II

Determination of Optimum Concentration of Ammonium Chloride in the Synthetic Medium

Temp.	0°		10°		20°		25°		30°		35°		40°		42°		43°	
Hrs.	24	98	37	45	24	46	24	36	24	83	24	72	46	77	24	48	24	45
Normality NH₄Cl	Count		Count		Count		Count		Count		Count		Count		Count		Count	
0.0118	2.6*	3.8*	20	21	96	120	40	56	102	242	109	99	204	146	—	—		
0.0128	1.8	2.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
0.0206	—	—	24	28	—	—	—	—	—	—	—	—	—	—	—	—		
0.0236	1.3	1.1	31*	39*	108	166	48	98	115	280	144	188	—	213	59	123		
0.0265	—	—	27	30	—	—	—	—	117	294	—	—	—	—	—	—		
0.0295	—	—	19	22	150*	224*	78	103	138	312	196	201	222	236	76	149		
0.0301	—	—	—	—	47	101	—	—	—	—	—	—	—	—	—	—		
0.0307	—	—	—	—	45	84	96	109	—	—	—	—	—	—	—	—		
0.0313	—	—	—	—	47	76	—	—	—	—	—	—	—	—	—	—		
0.0319	—	—	—	—	—	69	122*	156*	—	—	—	—	—	—	—	—		
0.0324	—	—	—	—	46	67	80	89	156	313	225	243	—	260	—	—		
0.0342	—	—	—	—	—	—	—	—	174	335	—	—	—	—	—	—		
0.0354	1.0	0.5	14	17	—	66	60	69	184*	369*	257	277	237	—	135	173		
0.0366			—	—	49	—	—	—	120	283	—	—	—	291	—	—		
0.0384			—	—	—	—	—	—	96	229	273*	314*	276	310	196	229	2.5	2.9
0.0413			10	12	—	—	49	56	85	226	202	186	288*	388*	238	283	2.6	3.0
0.0425					—	—	—	—	—	—	—	—	—	—	279*	342*	2.7	3.1
0.0431					—	—	—	—	—	—	—	—	—	—	—	—	3.1*	3.3*
0.0437					—	—	—	—	—	—	—	—	—	—	206	289	2.8	3.1
0.0442					—	—	—	—	—	—	—	—	—	—	—	—	2.7	3.0
0.0472					49	68	45	49	74	182	197	177	216	164	159	240	2.6	3.1
0.0590									67	177	143	168	198	142	143	186		

* Optimum.

Table III

The Effect of Ammonium Chloride upon the Growth of Yeast in Wort

Temperature	10		20		30		40		42
Normality of NH_4Cl	Count 36 hr.	Normality of NH_4Cl	Count 30 hr.	Normality of NH_4Cl	Count 22 hr.	Normality of NH_4Cl	Count 42.5 hr.	Normality of NH_4Cl	Count 25 hr.
0.000	185	0.000	210	0.000	230	0.000	680	0.000	29
0.0059	210	0.0118	240	0.0118	270	0.0236	795	0.0118	63
0.0088	222	0.0147	253	0.0236	352*	0.0259	825	0.0236	94
0.0118	235	0.0177	265	0.0294	232	0.02714	843	0.0294	157*
0.0129	248	0.0182	273	0.0341		0.0283	900*	0.0354	83
0.0135	260	0.0188	340*	0.0354	242	0.0294	720	0.0482	85
0.0141	321*	0.0194	258	0.0470	245	0.0354	692	0.0470	83
0.0147	245	0.0200	245	0.0588	244	0.0590	700	0.0588	84
0.0177	239	0.0236	233	0.0820	246	0.0826	713	0.0700	77
0.0354	226	0.0354	225	0.106	281*	0.1060	733	0.0820	72
0.0531	240	0.0590	220	0.118	235	0.1180	772*	0.0940	81
0.0590	256	0.0708	239	0.129	233	0.1416	685	0.1230	142
0.0649	269*	0.0767	242					0.140	111
0.0708	245							0.153	84
0.0826	232	0.0826	261*						
		0.0885	241						
		0.0896	236						

* Optimum

pounds pressure. After standing for three days to permit coagulated matter to settle out, the liquid was filtered and sterilized in live steam for thirty minutes.

The basal medium was Medium E[1] which for 30° has the following amounts of materials per 100 cc.: 0.188 g. NH_4Cl, 0.100 g. K_2HPO_4, 0.100 g. $CaCl_2$, 0.04 g. $CaCO_3$, 10 g. sugar.

The Determination of Optimum Concentrations of Ammonium Chloride in Medium E and in Wort

In Tables II, III and IV are given typical data showing the effects of various concentrations of ammonium chloride upon the growth of yeast in Medium E and in beer wort at several temperatures. It will be noted that with both media there are two optimum concentrations of the salt.

With both media the largest crops were obtained at 42°, a temperature considerably higher than that usually considered optimum for the growth of yeast. Slator[2] states that above 40° the enzymes are destroyed. In the synthetic medium the growth at 42° is as good as at 40° but there is a sharp break at 43°. It would seem than that with a properly adjusted medium of the given components that 40°-42° marks the temperature for the maximum growth of yeast and that a profound change takes place between 42° and 43°.

The ammonium salt may be said to act as a "temperature buffer". The term "thermal" death point of an organism may have as little general meaning as "optimum temperature" unless expressed in terms of the composition of the medium. The effect of ammonium salts upon the death rate of yeast and change in permeability to methylene blue[3] is being studied in this laboratory.

The data on wort confirm a previous statement[4] that whatever the role of bios may be in beer wort it is not the same as that of the ammonium salt.

In Table IV are assembled the optimal concentrations of the ammonium chloride for the media studied. In each instance the optimum normality of the salt is a linear function of the temperature, the appropriate equations being given in the table. By means of equations (1) and (2) may be calculated the optimum concentrations of the salt for a given temperature for the synthetic medium while equation (3) and (4) may be used for the beer wort employed in this work. Since latter medium may vary considerably in composition, depending upon the malt and method of mashing, these equations could not be promiscuously used. The equation should be determined for each sample. Similarly by means of the equations (5, 6, 7, and 8) may be calculated the optimum temperatures for a given normality of the ammonium salt. Equations (5) and (6) were used in calculating the data in Table I.

---

[1] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc., **43**, 191 (1921); Ind. Eng. Chem. **16**, 921 (1924); Fulmer: "Colloid Symposium Monograph," **2**, 204 (1924).

[2] Slator: J. Chem. Soc., **89**, 128 (1903).

[3] Miller: J. Phys. Chem., **24**, 564 (1920); Fraser: J. Phys. Chem., **25**, 1; Fulmer: 10 (1921).

[4] Fulmer, Sherwood and Nelson: Ind. Eng. Chem., **16**, 921 (1924).

TABLE IV

The Effect of Ammonium Chloride upon the Growth of Yeast in Medium E—Second Maximum

Temperature	10		20		30		40
Normality of NH_4Cl	Count 30 hr.	Normality of NH_4Cl	Count 35 hr.	Normality of NH_4Cl	Count 28 hr.	Normality of NH_4Cl	Count 30 hr.
0.0000	48	0.000	58	0.000	61	0.000	67
0.059	53	0.059	65	0.118	75	0.118	76
0.118	61	0.118	71	0.177	84	0.177	84
0.1298	72	0.1475	80	0.2265	89	0.2265	91
0.1475	80	0.177	86	0.236	105*	0.236	94
0.1534	92*	0.182	89	0.295	84	0.265	97
0.1593	79	0.194	100*	0.354	76	0.278	111*
0.1652	60	0.206	88	0.472	63	0.287	79
0.177	55	0.236	65	1.118	58	0.295	72
0.236	40	0.354	56	1.483	50	0.354	65
0.2950	38					0.4720	59

* Optimum.

TABLE V

Optimum Concentrations of Ammonium Chloride in Medium E and in Wort

	Medium E		Wort	
Temp.	I(1)	II(2)	I(3)	II(4)
0	0.0118	———		
10	0.0236	0.1534	0.0141	0.0649
20	0.0295	0.1940	0.0188	0.0826
25	0.0319	———	———	———
30	0.0354	0.236	0.0236	0.106
35	0.0383	———		———
40	0.0413	0.278	0.0283	0.118
42	0.0425	———	0.0294	0.123
43	0.0431	———	———	

N = normality of ammonium chloride
t = temperature

Medium E

[1] $N_1 = 0.00057t + 0.0179;\ t_1 = \frac{N - 0.0179}{0.00057}$

[2] $N_2 = 0.0042t + 0.111;\ t_2 = \frac{N - 0.111}{0.0042}$

Wort

[3] $N_1 = 0.0090 + 0.0050t;\ t_1 = \frac{N - 0.0090}{0.0050}$

[4] $N_2 = 0.0475 + 0.00177t;\ t_2 = \frac{N - 0.0475}{0.00177}$

The Optimum Concentrations of K_2HPO_4, $CaCl_2$ and $CaCO_3$

Data showing the effect upon the growth of yeast at several temperatures of various concentrations of K_2HPO_4, $CaCl_2$ and $CaCO_3$ in Medium E are found in Tables VI, VII and VIII. The results confirm our previous findings.[1]

TABLE VI

Growth of Yeast, varying K_2HPO_4

Normality K_2HPO_4	25°C. I = 1 Count 30 hr.	30°C. I = 1 Count 66 hr.	30°C. I = 1 Count 42 hr.	35°C. I = 1 Count 24 hr.	40°C. I = 1 Count 24 hr.	40°C. I = 1 Count 72 hr.
0.0000	180	93	60	27	26	91
0.00232	222	227	162	172	98	183
0.003480	246	280	165	181	126	241
0.00464*	261	305	205	190	159	269
0.00696	260	302	204	189	158	267
0.00928	259	304	203	187	157	268
0.01160	261	303	202	188	158	269
0.01392	262	302	203	187	159	267

* Optimum.

TABLE VII

Growth of Yeast, varying $CaCl_2$

Normality of $CaCl_2$	25°C. I = 1 Count 24 hr.	25°C. I = 1 Count 48 hr.	30°C. I = 1 Count 72 hr.	30°C. I = 1 Count 48 hr.	35°C. I = 1 Count 42 hr.	35°C. I = 1 Count 98 hr.	40°C. I = 1 Count 24 hr.	40°C. I = 1 Count 48 hr.
0.000	61	92	217	186	157	202	160	210
0.00180	73	106	235	198				
0.00360	91	117	247	202	161	257	209	269
0.00540	105	129	289	246				
0.00720	130	136	295	266	177	260	212	272
0.00900	140	156	304	290				
0.0108	158	173	312	298	191	274	226	285
0.0126	219	196	310	310				
0.01440	256	218	318	318	211	278	245	299
0.01620	286	278	335	342	232	286	251	
0.01800*	379	334	386	388	255	319	275	325
0.0216	375	333	387	388	253	318	276	328
0.0217	378	335	388	389	254	315	274	326
0.0324	376	335	387	389	255	318	275	324
0.0360					254	317	276	

* Optimum.

---

[1] Refers to first reference given on page 742.

TABLE VIII

Growth of Yeast, varying $CaCO_3$

Normality of $CaCO_3$	25°C. I = 1 Count 32 hr.	30°C. I = 1 Count 48 hr.	35°C. I = 1 Count 36 hr.	40°C. I = 1 Count 46 hr.
0.000	42	130	65	70
0.0040	115	179	170	196
0.0060	125	298	192	210
0.0080*	170	371	220	251
0.0100	100	238	180	215
0.0120	80	226	164	190
0.0160	65	206	150	140
0.020	52	186	148	139
0.024	51	175	139	

* Optimum.

It will be noted that the optimum concentrations of the salts above studied do not vary with temperature as do those for the ammonium chloride. In Table IX are given the concentrations for the best possible medium for the growth of yeast at any temperature with the given components.

TABLE IX

The Concentrations of Salts in Medium E Optimum for Any Temperature

Salt		Normality	Grams per 100 cc.
NH_4Cl		(1) 0.0179 + 0.00057t	0.0960 + 0.60306t
		or	or
		(2) 0.111 + 0.0042t	0.595 + 0.675t
K_2HPO_4	(anhyd)	0.00464	0.0260
$CaCl_2$	(anhyd)	0.01800	0.100
$CaCO_3$	(ppted)	0.0080	0.040

The Growth of Yeast in Various Media

In Table X will be found data showing the growth of yeast in wort without added ammonium chloride while data on the growth of yeast in wort to which had been added the optimum concentration of the ammonium salt for each temperature will be found in Table XI.

TABLE X

Growth of Yeast in Wort without NH_4Cl

0°		10°		20°		30°	
Time (Hours)	Count	Time	Count	Time	Count	Time	Count
28	2.2	26	13	17	57	7	15
35	2.7	29	19	19	92	11	71
48	3.9	36	35	21	149	13	153
52	4.3	40	53	23	243	14	225
64	4.4	52	128	25	281	23	677
76	4.6	62	162	29	792	29	1050
		77	164	39	1165	35	1092
				48	1190	40	1197
				63	1205	46	1205
						49	1220
						59	1215
						73	1223

40°		42°		43°	
Time (Hours)	Count	Time	Count	Time	Count
6	4.5	9	53	12	1.6
8	25	10	83	18	2.2
9.5	67	11	131	24	2.8
12	223	13	308	30	3.6
13	320	15	316	38	3.7
14	505	17	340	45	3.8
23.5	837	21	355	68	3.8
29	872	33	408		
37	1342	41.5	521		
48	1345	56	625		
60	1332	68	630		
72	1342				

TABLE XI

Growth of Yeast in Wort with Optimum Concentrations of NH_4Cl

	10°		20°		30°		40°		42°	
	Count		Count		Count		Count		Count	
Time (Hours)	1st Opt.	2d	1st Opt.	2d	1st Opt.	2d	1st Opt.	2d	1st Opt.	2d
8					29	25				
9									64	59
10					56	54	131	113		
11					87	82	209	178	161	146
12	3.5	3.4			130	122	332	277	255	228
13									406	356
15	4.8	4.6					1107	980		
17	6.0	5.7	72	63						
18			92	83						
19	7.2	6.8	119	107						
21			196	175						
21.5					1437	1300				
23									600	525
25			384	342						
25.5							1330	1200		
26	15	14.0								
32	28	26								
34			1059	1040	1470	1390				
35									652	617
43			1301	1180						
45	109	98								
47							1465	1380		
48									667	655
50	153	133								
55			1404	1270						
59					1510	1395			670	662
62	237	206								
67			1449	1296						
69							1705	1565		
70					1515	1400				
74	244	210								
75			1444	1300						
81	246	212					1710	1560	665	660

In Table XII are given the data showing the growth of yeast on the synthetic media. The figures in the columns marked A were obtained by using Medium E with the optimum concentration of ammonium salt for each temperature while in the experiments designated B Medium E was used with the concentration of the ammonium salt optimum for 30°.

TABLE XII

Growth of Yeast in Medium E. A. Opt. for Each Temp. B. Opt. for 30°

Temp.	0°	10°		20°		30°		40°		42°		43°
Time	A	A	B	A	B	A	B	A	B	A	B	A
6												
7												
8									11	13	7.5	
9										17		
10									21		13.5	
11						30	33	43	28	23		
12						45	45	63	38			1.5
13								91		41	26	
14						77	77					
15			3.0			110	110	112		70		
16						137			97		55	
17				34	24					131		
18					24							1.8
19			4.2	49								
21				74	42					162		
22								169				
23			5.5	111								
24					72						89	
25				128								
26		11										
28	2.1				80							
29		16		149								
30			12									
32									144			2.7
33										258		
34								223				
35	2.6					156	156					
36		28										
37												

TABLE XII (Continued)

Growth of Yeast in Medium E. A. Opp. for each Temp. B. Opt. for 30°

Temp.	0°	10°		20°		30°		40°		42°		43°
Time	A	A	B	A	B	A	B	A	B	A	B	A
38												3·4
39		42	18	224		191	192				132	
40												
41					174					332		
42									188			
43						254	258					3·5
45								395				
46						261						
48	3.6			280			261					
50					184							
51											139	
52	3.8	105										
54						274						
55			37									
56									195	349		
58								393				
59							274					
60												
62		134		283								
63											138	
64	4.2		67									
65					205	270				345		
68								399				3·4
69									196			
71							270					
72			69									
73								398				
75	4.1	137			203				202			

The data above presented permit an analysis of three growth phases of yeast in various media at several temperatures. Buchanan[1] describes and discusses in detail seven growth phases in a culture of a microorganism.

1. Initial Stationary Phase during which the number of cells remains constant.

2. Lag Phase or Positive Growth Acceleration Phase in which the "average rate of increase in numbers per organism increases with the time".

3. The Logarithmic Growth Phase during which "the rate of increase per organism remains constant".

---

[1] Buchanan: J. Infect. Dis., **23**, 109 (1918).

3. Phase of Negative Growth Acceleration in which "the rate of growth per organism decreases".

5. Maximum Stationary Phase during which "there is practically no increase in the numbers of organisms".

6. Phase of Accelerated Death in which the numbers of cells is "decreasing with increasing rapidity".

7. Logarithmic Death Phase during which the "rate of death per organism remains constant".

The Logarithmic Growth Phase of Yeast in Several Media at Different Temperatures

During the logarithmic or maximum rate of growth the number of cells increases a certain fraction of itself each instant, that is if C = count

$$(1)\quad \frac{dC}{dt} = kC$$

$$(2)\quad \int_{C_1}^{C_2} \frac{dC}{C} = k \int_{t_1}^{t_2} dt$$

and

$$(3)\quad \log C_2 - \log C_1 = k(t_2 - t_1)$$

During this phase of growth the generation time, that is, the time required for one cell to become two will be:

$$(4)\quad \text{g.t.} = \frac{\log 2}{k}$$

From the growth data previously given values of k were obtained as the slope of the straight lines resulting from the graph of log 10 C plotted against time. The following discussion will deal then with the effect of temperature upon the value of *k* per various media. A summary of such values is given in Table XIII.

TABLE XIII

Values of *k* for Various Media at Different Temperatures

Temperature	Wort No NH_4Cl added	Wort 1st Optimum NH_4Cl	Wort 2d Optimum NH_4Cl	Medium E Optimum for 30°	Medium E Optimum for each Temperature
0	0.0122	0.0453	0.0443		0.0113
10	0.0430	0.1092	0.1068	0.0324	0.0405
20	0.1035	0.1780	0.1740	0.0777	0.0883
30	0.1686	0.2051	0.1992	0.1361	0.1361
40	0.1936	0.2005	0.1964	0.1316	0.1452
42	0.1923			0.1098	0.1239
43	0.0180				0.0143

In Table XIV the values of *k* for the various media are compared to that for wort as standard.

TABLE XIV

The Value of K for Various Media Where $K = \frac{k(\text{Medium Used})}{k(\text{Wort})}$

Temperature	Wort 1st Optimum NH_4Cl	Wort 2d Optimum NH_4Cl	Medium E Optimum for 30°	Medium E Optimum for each Temperature
0	3.71	3.63	——	0.93
10	2.54	2.48	0.75	0.94
20	1.72	1.68	0.75	0.85
30	1.22	1.18	0.807	0.807
40	1.03	1.01	0.54	0.75
42	——	——	0.57	0.64
43	——	——	——	0.79

The increase in growth rate in wort due to the addition of the optimum concentrations of the ammonium chloride is especially striking at the lower temperatures. The above points are shown clearly on the graphs in Fig. 1 where the values of *k* are plotted against temperature.

With a rise in temperature the advantage of the salt decreases with practically no effect at 40°. The two optimum concentrations for the wort give practically identically results. In the synthetic medium again is seen the advantage of using the optimum concentrations for each temperature as compared to results obtained by use of a medium optimum for the one temperature of 30°.

The Temperature Coefficients for the Growth of Yeast in Several Media at Various Temperatures

Using the values for *k* found in Table X the temperature coefficients are calculated on the usual basis where $Q_{10} = k(t_1 + 10)/k(t_2)$. Values for Q_{10} are listed in Table XVI. In the same table are listed values for "μ" calculated from the van't Hoff equation as follows:

$$(5) \quad 2.303 \log \frac{K_0}{K_1} = \frac{\mu}{2}\left(\frac{T_1 - T_0}{T_1 T_0}\right)$$

In every instance through a range of 10-40 there is a smaller "spread" of values for Q_{10} in cases where optimum conditions are maintained compared to values for unadjusted media. With wort the differences in value of Q_{10} for adjusted and non-adjusted medium is greatest at the lower temperatures.

In Table XVII are found average values of Q_{10} obtained by various investigators.

TABLE XVI

Values of Q_{10} and of μ for Various Media

Medium	W_0		W_1		E_0		E_1		Slator (6)	
Temperature	Q_{10}	μ	Q_{10}	μ	Q_{10}	μ	Q_{10}	μ	Q_{10}	μ
10	3.52	12,500	2.43	8,600			3.52	12,500	5.6	19,900
15							(2.8)	10,300	3.8	14,000
20	2.41	9,800	2.41	9,800	2.40	9,800	2.18	8,800	2.8	11,400
25							(1.8)	7,600	2.2	9,300
30	1.63	7,100	1.63	7,100	1.75	7,600	1.54	6,700	1.9	8,300
35							(1.3)	5,900	1.6	7,200
40	1.15	5,300	1.14	5,300	0.966	4,600	1.07	5,000	(1.3)	6,000
42	0.99	4,600	0.98	4,600	0.834	3,900	0.85	4,000		
43	0.093						0.115			
ΔQ_{10} (10-40)	2.53		1.45				2.67		4.3	
ΔQ_{10} (20-40)	1.25		1.26		1.43		1.11		1.5	

W_0 = Wort without ammonium chloride
W_1 = Wort with optimum concentration of ammonium chloride
E_0 = Medium E optimum for 30°
E_1 = Medium E optimum for each temperature

TABLE XVII

Average Values of Q_{10}

Investigator		Temperature Range	Average Q_{10}
Slator[1]		10-35	2.97
Herzog[2]		14-28	2.88
Aberson[3]		12-33	2.72
Sherwood and Fulmer	W_0	10-40	2.18
	W_1	10-40	1.90
	E_1	10-40	2.05

W_0 = wort without ammonium chloride.
W_1 = wort with optimum concentration of ammonium chloride.
E_1 = medium E optimum for each temperature.

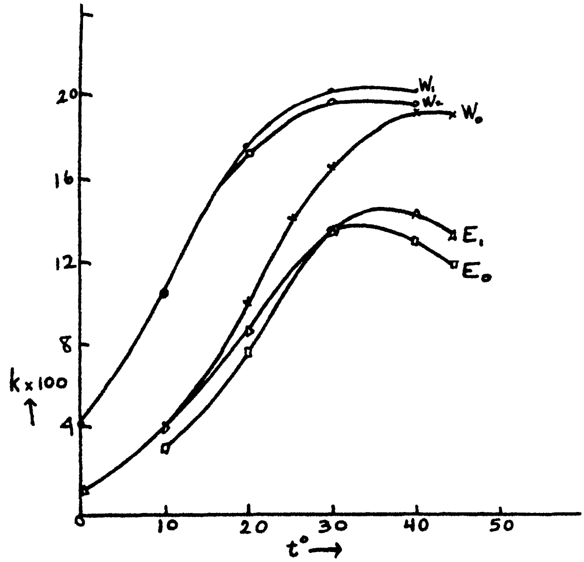


FIG. 1

An examination of this table shows the widely differing values for Q_{10} obtained by various investigators of yeast growth. It is evident that the lowest average values obtained are typical of media whose composition has been adjusted in an appropriate manner for each temperature thus eliminating certain variables discussed in the Introduction.

---

[1] Slator: J. Chem. Soc., **89**, 128 (1903).
[2] Herzog: Z. physik. Chim., **37**, 149 (1902).
[3] Aberson: Rec. Trav. chim., **22**, 78 (1903).

The Phase of Negative Growth Acceleration and the Maximum Stationary Growth Phase of Yeast

In studies on temperature coefficients for the growth of yeast use has usually been made of the phase, the logarithmic phase. However environment may not influence the growth phases equally or even in the same direction. For example, with reference to the logarithmic phase and the Maximum Stationary Phase or "total crop" a change of environment may cause one of nine effects as follows:

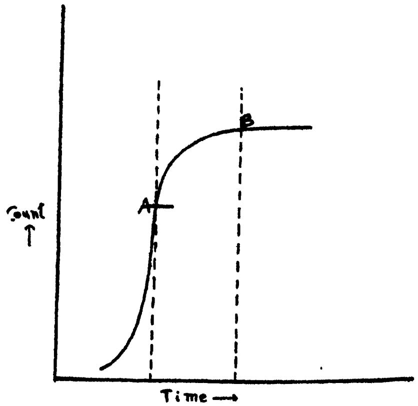


FIG. 2

TABLE XVIII

Logarithmic Phase	Total Crop
I. Increase	No effect
II. Increase	Decrease
III. Increase	Increase
IV. Decrease	No effect
V. Decrease	Decrease
VI. Decrease	Increase
VII. No effect	No effect
VIII. No effect	Decrease
IX. No effect	Increase

From the graphs of growth data given above a study may be made of the effect of ammonium chloride and of temperature upon the phase of negative growth acceleration and the total or maximum crop. The former phase is represented by the count at the inflection of the curve between the logarithmic phase and the maximum stationary phase, that is, the count at which the growth just ceases to be logarithmic. These points are designated on a typical curve on Fig. 2. Values for the above functions are given in Table XIX.

TABLE XIX

Maximum Crop and Critical Count for the Growth of Yeast in Various Media at Several Temperatures

Medium	W_0		W_1		W_2		E_0		E_1	
Temp.	A	B	A	B	A	B	A	B	A	B
0									4.2	4.2
10	102	161	153	246	133	212	37	69	105	137
20	290	1218	384	1442	342	1300	80	203	128	282
30	1245	1350	1437	1515	1300	1400	156	270	137	280
40	950	1555	1380	1710	1200	1560	97	202	223	394
42	450	622	600	665	525	660	89	138	131	343
43									3.3	3.4

A = Inflection count.
B = Total crop.
W_0 = Wort with NH_4Cl.
W_1 and W_2 = Wort with 1st and 2d optimum NH_4Cl.
E_0 = Medium E optimum for 30°.
E_1 = Medium E with optimum NH_4Cl.

The data show that the effect of the ammonium salt falls into class III given in Table XVIII that is the salt increases both the logarithmic growth rate and the total crop. It is also apparent that the salt leads to an increased count at the inflection point in the logarithmic curve. However, the figures given in Table XX show that the inflection count and the total crop are not increased equally. At 20° in all the media used with the possible exception of E_1 the phase of negative growth acceleration is more extended than at any other temperature. The maximum logarithmic growth rate, inflection count, and total crop occur at 40° for all the media used except Medium E optimum for 30°.

TABLE XX

Ratio of "Inflection Count" to "Total Crop", B/A

	Medium				
Temp.	W_0	W_1	W_2	E_0	E_1
10	1.6	1.6	1.6	1.8	1.3
20	4.6	3.8	3.8	2.5	2.2
30	1.1	1.1	1.1	1.7	2.0
40	1.6	1.2	1.3	2.1	1.8
42	1.4	1.1	1.2	1.6	2.6

Summary

1. A detailed study has been made upon the growth of yeast at various temperatures in several media.

2. The optimal concentrations of ammonium chloride in the synthetic medium have been formulated.

3. Temperature coefficients for the growth of yeast were determined in media adjusted to optimum concentrations for each temperature and compared to those obtained in media not so adjusted.

4. A quantitative study was made of the phase of negative growth acceleration and the maximum stationary growth phase of yeast in several media at different temperatures.

MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE. PART III. THE MEAN LIFE OF ACTIVITY IN ILLUMINATED CHLORINE*

BY ABRAHAM LINCOLN MARSHALL

It was suggested in Part I of this series of papers[1] that it might be possible to distinguish between the two types of mechanism which have been advanced to account for the photochemical reaction between hydrogen and chlorine by a re-investigation of the rate of decay of activity in illuminated chlorine. Chlorine atoms as postulated in the Nernst mechanism should have a relatively long life while excited chlorine molecules according to our present views might have a mean life period of the order of $(10)^{-6}$ sec.

Bodenstein and Taylor[2] investigated this problem and were unable to detect any enhanced reactivity in chlorine 0.00065 sec. after illumination. They illuminated chlorine with light from a 25 candle power Osram lamp placed 30 cm. from the reaction system. The chlorine after illumination was passed thru a bent capillary into a stream of hydrogen. The capillary was blackened to prevent light from reaching the mixed gases. The capillary used by them was of 0.3 mm. radius, 20 mm. long with a volume of 0.0065 cc.

Gohring[3] has analysed the results of Taylor and showed them to be consistent with the Nernst mechanism. The chlorine which they used was electrolytic and is assumed to contain 0.1 percent of oxygen. From this value Gohring calculates the concentration of atomic chlorine in the steady state to be $6.9(10)^{-18}$ mol-litre and the half life period as 0.00012 second. This would give rise in Taylor's experiments to an undetectable amount of hydrogen chloride.

Let E = radiation of frequency ν absorbed per second.
V = volume of the vessel.
Z_{11} = number of impacts per second one chlorine atom makes with all the other chlorine atoms.
Z_{12} = number of impacts per second one chlorine atom makes with oxygen molecules present in the gas.
N_1 = number of chlorine atoms—c.c.
N_2 = number of oxygen molecules—c.c.
$1/2 N_1 Z_{11}$ = total impacts between chlorine atoms per c.c.—second.

$$Z_{11} = kN_1$$

where $k = \Omega\pi\sigma_1^2\sqrt{2}$ and Ω_1 = velocity of chlorine atoms.
σ_1 = diameter of chlorine atoms.

$$Z_{12} = k_1 N_2$$

$$k = 2\sigma_{AB}^2\sqrt{\frac{m_1 + m_2}{m_1 m_2} \cdot 2\pi RT}$$

---

* Contribution from the Laboratory of Physical Chemistry, Princeton Univ.

[1] J. Phys. Chem., **29**, 842 (1925).

[2] Z. Electrochem., **22**, 202 (1916).

[3] Z. Electrochem., **27**, 516 (1921).

$k_1N_1N_2$ = total impacts between atomic chlorine and oxygen. Gohring calculates $1.5(10)^{-8}$ of these impacts to be effective,

$$\text{then}\quad \frac{dN_1}{dt} = 2\,\frac{E}{h\nu}\cdot\frac{1}{V} - N_1^2 - 1.5(10)^{-8}\,K_1N_1N_2$$

in the steady state—

$$2\,\frac{E}{h\nu}\cdot\frac{1}{V} = k\,N_1^2 + 1.5(10)^{-8}\,k_1N_1N_2$$

For the moment let us neglect the deactivation caused by impacts between chlorine atoms; then in the steady state—

$$2\,\frac{E}{h\nu}\cdot\frac{1}{V} = 1.5(10)^{-8}\,k_1N_1N_2$$

$$\bar{N}_1 = \frac{2E}{h\nu V k_1 N_2 \times 1.5(10)^{-8}}$$

$$= \text{concentration of Cl in steady state.}$$

The problem now is to calculate the concentration of Cl 1/1600 second after the illumination is cut off.

$$-\frac{dN_1}{dt} = 1.5(10)^{-8}\,k_1N_1N_2$$

$$\ln\frac{\bar{N}_1}{N_1} = 1.5(10)^{-8}\,k_1N_2t$$

$$k_1 = 2(2.55)^2(10)^{-16}\sqrt{\frac{67}{32\times 35}\times 82.15(10)^6\times 2\pi\times 300}$$

$$= 1.25(10)^{-10}$$

$$N_2 = 0.1\ \text{percent} = \frac{6(10)^{23}}{22{,}400\times 7{,}600} = 2.68(10)^{16}$$

$$E = 10^{-8}\ \text{g. cals.—sec.}$$

$$= 4.18(10)^4\ \text{ergs.—sec.}$$

$$h\nu = 3.93(10)^{-12}\ \text{ergs. for}\ \lambda = 500\mu\mu.$$

$$V = 200\ \text{c.c.}$$

$$t = 1/1600\ \text{sec.}$$

$$\log N_1 = \log\frac{2\times 4.18(10)^4}{3.93(10)^{-12}\times 200\times 1.25(10)^{-10}\times 2.68(10)^{16}\times 1.5(10)^{-8}} - \frac{1.5(10)^{-8}\times 1.25(10)^{-10}\times 2.68(10)^{16}}{2.33\times 1600}$$

$$= 10.318 - 1.36$$

$$= 8.96$$

$$N_1 = 9.1(10)^8\ \text{atoms Cl—c.c.}$$

If each atom is responsible for the formation of 10^6 molecules of HCl

$$N_{HCl} = 9.1(10)^{14} \text{ molecules} = 0.0034 \text{ percent HCl}$$

which is an undetectable amount under the experimental conditions of Bodenstein and Taylor.

Warburg[1] has also treated this problem neglecting the effect of oxygen and concludes that one should expect a considerable amount of hydrogen chloride to be formed. Assuming we are dealing with pure chlorine the concentration of atomic chlorine in the steady state is given by the equation $\bar{N}_1 = \sqrt{\frac{2E}{h\nu Vk}}$ the rate of decay of activity is $-\frac{dN_1}{dt} = kN_1^2$ and the concentration N_1 of atomic chlorine at time *t* after illumination is given by $1/N_1 - 1/\bar{N}_1 = kt$

$$k = \Omega_1\pi\sigma_1^2\sqrt{2} = 14{,}500\sqrt{\frac{300}{35}\cdot\frac{22}{7}}\cdot 4(10)^{-16}\sqrt{2} = 7.55(10)^{-11}$$

$$N_1 = \sqrt{\frac{2 \times 4.18(10)^4}{3.93(10)^{-12} \times 200k}} = \sqrt{1.41(10)^{24}} = 1.19(10)^{12}$$

$$1/N_1 = 4.7(10)^{-14} + 8.4(10)^{-13}$$

$$N_1 = 1.1(10)^{12} \text{ atoms of chlorine}$$

It will be observed that in this calculation practically none of the atomic chlorine has combined in 1/1600 second, and this on the assumption that every impact of chlorine atoms with one another leads to combination. From analogy with the observed results on the combination of atomic hydrogen and atomic bromine, one would only expect about one in every thousand impacts to be fruitful.

If the analysis given by Gohring and Warburg is correct it should be possible to obtain very considerable amounts of hydrogen chloride in an experiment of this nature provided pure chlorine free from inhibitors for the reaction is used and is subjected to intense illumination.

Experimental

A diagram of the apparatus used is given in Fig. 1. The whole set up between the capillary *H* and the liquid air trap *C''* was so arranged that it could be surrounded by a furnace and heated to 300°-400°C. While the apparatus was being heated a stream of chlorine gas from an electrolytic generator was passed thru the apparatus. On several occasions the capillary *H* was cooled in liquid air to block it with solid chlorine and the whole set up was evacuated with a diffusion pump. This treatment was continued for several days to ensure the complete removal from the system of all impurities which were volatile or were capable of reacting with chlorine. In the subsequent experiments inhibitors of the type described by Chapman and Burgess[2] due to albuminous material on the walls of the vessel were absent. This procedure is an improvement over that previously used since it greatly shortens the time necessary to clean up the apparatus and makes it more probable that a proper cleansing has been accomplished.

---

[1] Z. Electrochem., **27**, 139 (1921).

[2] J. Chem. Soc., **89**, 1399 (1906).

Only two stopcocks were used in the entire apparatus and these never came in contact with chlorine and were protected by liquid air traps from the rest of the system so that impurities from the grease used for lubrication might not diffuse into the carefully purified reaction system.

The capillary *B* thru which the chlorine gas was forced after illumination was made of a special ruby glass supplied by the Corning Company, which sealed directly to G702P glass of which the whole set-up was constructed. The capillary was constricted to the required diameter by a process of trial and error; the two capillaries used in this investigation were about 8 mm. long and had volumes respectively of 0.00018 and 0.00034 cc. These volumes were determined by weighing the amount of mercury required to fill the capillary. The part *A* consisted of a quartz to glass graded seal with a quartz window at the end. The distance from the window to the capillary opening was 5 cm. An Hanovia quartz mercury arc was used as a source of illumination and was contained in a black box with a diaphragm attached with an opening the size of the window at *A*. The end of *A* was placed against the opening in the diaphragm, and the arc was 4 cm. from *A*. It consumed 3 amps. at 60 volts.

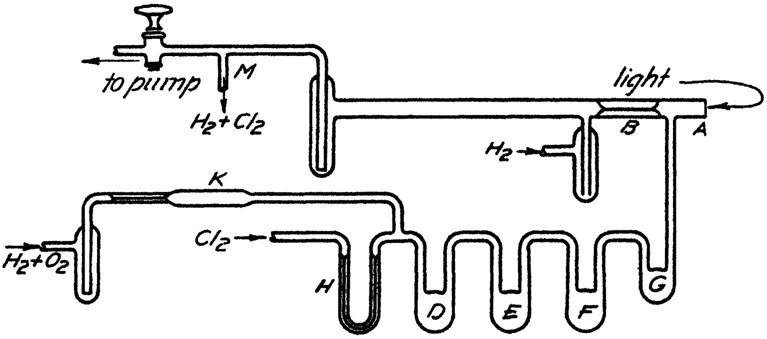


FIG. 1

The whole apparatus on the hydrogen side of the capillary was painted black after the preliminary baking out process and the experiments were carried out in a darkened room free from all stray light.

The chlorine used was taken from a cylinder of electrolytic chlorine. It was washed with water and passed over heated glass powder to decompose any oxides of chlorine present. While collecting the chlorine in the container *D* the whole apparatus was evacuated the capillary *B* having been shunted by a glass by-pass which was later sealed off. The chlorine was condensed in liquid air any oxygen present being removed by the pump. After filling *D* the apparatus was sealed off at the capillary *H* from the source of chlorine; container *E* was cooled in liquid air and *D* with a CO_2-ether mixture and chlorine distilled into *E* in a high vacuum. Due to the poor heat exchange consequent on the high vacuum conditions the chlorine in *D* remained solid thruout the distillation. The first fraction of the distillate was collected. A similar distillation was made from *E* to *F*. The chlorine collected in *F* was kept in an ice bath which gave a chlorine pressure of 3.7 atmos. This pressure was used to drive the chlorine at a high rate of flow thru the capillary *B* after illumination. Electrolytic hydrogen was led in thru the liquid air trap *C′* and the mixture of hydrogen and chlorine passed out at *M* into a solution of potassium iodide.

The chlorine as prepared above was exceedingly dry and it became necessary to moisten it. This was accomplished by first collecting some water in the container *G*, which was cooled in liquid air, before the chlorine was collected. The water was made by passing hydrogen containing some oxygen over a piece of heated quartz tubing *K* which was sealed into the apparatus with graded seals. The combustion was carried out at low pressures to avoid an explosion.

The protection given by the liquid air traps was necessary to prevent any contamination from entering the system after baking out; the traps were in the furnace in the preliminary heat treatment. During the experiments the water was kept at room temperature.

Results

The first series of experiments was made with dry chlorine. Four experiments were made with chlorine flowing at a rate of 0.55 cc.—sec. corresponding to a time of 0.00033 sec. for passage thru the capillary. The iodine released by the chlorine was titrated with N/4 thiosulfate and methyl red was used as an indicator for the acid titration. All the solutions used were carefully neutralised before an experiment so that a drop of N/10 acid or alkali was sufficient to produce a marked change in the indicator. In these experiments the solution remained neutral and no trace of acid was found. The time of passage thru the capillary was decreased to 0.00020 sec. by increasing the chlorine temperature to 20°C. Still no acid was detected.

It was then decided to wet the chlorine before illumination. A series of experiments with moist chlorine passing thru the capillary into hydrogen 0.00030 sec. after illumination produced no detectable amount of hydrogen chloride.

These results with pure chlorine were entirely unexpected in the light of the previous discussion and might lead one to conclude that the Nernst mechanism, on which that analysis was based, was incorrect. The effect of the glass walls has however not been considered and it is quite possible that these may be catalysing the recombination of the chlorine atoms. It will apparently be necessary to resort to some other method of experimentation to settle this point. The author has suggested a method of attack[1] involving a quantitative study of the rate of reaction at low pressures and being a continuation of previous work[2]. If the mechanism involves chlorine atoms it should be possible to calculate the rate of reaction as a function of the pressure from a knowledge of the quanta absorbed and the rate of diffusion of the atoms to the surface of the container where they are removed from the system.

---

[1] Trans. Am. Electrochem. Soc., Spring Meeting (1926).

[2] J. Phys. Chem., 29, 1453 (1926).

Summary

The experiments of Bodenstein and Taylor on the mean life of reactivity in illuminated chlorine have been repeated using an improved technique. Pure chlorine was used and passed into hydrogen $3(10)^{-4}$ sec. after intense illumination by a quartz mercury arc. *No reactivity was detectable.*

This result was directly contrary to a mathematical analysis based on the Nernst atomic mechanism which predicted a large reaction. Only two possibilities seem to arise: either this mechanism is incorrect and it is necessary to assume a mechanism involving excited chlorine molecules, or the walls of the capillary remove the chlorine atoms by causing their recombination. Further experimentation is necessary to reach a decision and a possible method of attack is pointed out.

Princeton, N. J.

A STUDY OF THE PRECIPITATION OF MASTIC SUSPENSOIDS*

BY H. V. TARTAR AND CARL Z. DRAVES

Introduction

None of the generalizations dealing with the precipitation of colloids by electrolytes, have been reduced to exact quantitative form. It has long been known that two of the primary factors which determine the precipitation of a colloid of the suspensoid type (hydrophobic colloid) are the concentration and the valence of the ion of the electrolyte in solution which has an electric charge opposite in sign to that of the colloidal particles. Although there is abundant evidence in the literature that hydrogen and hydroxyl ions may be strongly adsorbed but scant consideration has been given, in work dealing with the precipitation of colloids, to the full effect of these ions.

Michaelis and Timenez-Diaz[1] have pointed out very clearly that the concentration of hydrogen-ion (or hydroxyl-ion) may be quite as important in its effect as that of the ions of the added electrolyte. For example, they found that the concentration of potassium salt just sufficient to precipitate a negative suspensoid varies widely with the hydrogen-ion concentration of the dispersion medium. Michaelis and his coworkers[2] used negative suspensoids for which the minimal concentration of the salt required for precipitation at a given Sörensen value (pH) is but slightly affected by the character of the negative ion from the added electrolyte. This permitted the use of Sörensen buffer solutions for effecting precipitation at varying hydrogen-ion concentraions. The results of this work, using congo red and colloidal mastic, showed that the relationship between hydrogen-ion concentration and salt concentrations was represented approximately by the following equation for an equilateral hyperbola:

$$\left[\log \frac{(H_o{}^+)}{(H+)}\right] \left[\log \frac{(i_o)}{(i)}\right] = K$$

in which (i) represents the salt concentration which is just sufficient to cause precipitation and (H^+) the simultaneous value of the hydrogen-ion concentration in the same experiment. $(H_o{}^+)$ is a constant which is equal to the hydrogen-ion when precipitation is effected with hydrochloric acid alone; while (i_o) is the limiting value of the salt concentration necessary for precipitation as the solution is made more and more alkaline; K is a constant which must be determined from the experimental values. This equation expresses the fact that the concentration of salt required for precipitation increases rapidly with decrease in the hydrogen-ion concentration of the dispersion medium.

---

* Contribution from the Chemical Laboratory, University of Washington.

[1] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921).

[2] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921); Michaelis and Hirabayashi: 30, 209 (1922).

Tartar and Gailey[1], in a preliminary paper, found that for the negative suspensoids, mastic and gamboge, widely varying concentrations of salts yielding the same cation but different anion were required for precipitation; also that the variation in hydrogen-ion concentration, due to hydrolysis of the salts used, was as great as the variation of the salt concentrations. On the other hand, when the experiments were made using the same concentrations of the different salts as was required for potassium chloride alone, together with a sufficient amount of the acid with anion corresponding to that of the salt employed, all the precipitations occurred at approximately the same Sörensen value (pH).

Tartar and Gailey also found that different common acids when used alone produced precipitation of mastic or gamboge at the same hydrogen-ion concentration regardless of the valence of the anion. The data of Michaelis and Hirabayashi[2] also showed that with either acids alone or mixtures of salts and acids, the anion (with the exception of the sulfosalicylate-ion which is very antagonistic) has only a slight effect on the precipitation of congo red and mastic suspensoids.

In each investigation referred to above on the precipitation of colloidal mastic, the conditions were simplified and made uniform by using a carefully prepared sol. As yet, no satisfactory study has been made of the effects of using different samples of the gum, of varying the concentration or dispersity of the sols, on the precipitation with electrolytes at different hydrogen-ion concentrations. Neisser and Friedemann[3] "showed that the precipitation value of salts with univalent cations is less the more concentrated the emulsion (mastic) while with divalent and trivalent cations the precipitation value decreases slightly as the concentration of colloid decreases". Bechhold[4] found that the rate of precipitation of mastic with electrolytes depends, within certain limits, upon the concentration of the sol. Odén[5], in attempting to separate colloidal mastic particles of varying size by fractional precipitation, investigated the effect of particle size on the critical concentration of electrolyte for precipitation and was unable to prove that there was a relationship of particle size to precipitation. Burton and Bishop[6] enunciated the rule as a result of their experiments on the effect of the dilution of mastic sol that "for univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration, this increase being very rapid with low concentrations of colloid". In all these investigations by different workers, however, the marked influence of the hydrogen-ion concentration of the dispersion medium was not taken into consideration.

---

[1] Tartar and Gailey: J. Am. Chem. Soc., **44**, 2212 (1922).

[2] Michaelis and Hirabayashi: Kolloid-Z., **30**, 209 (1922).

[3] Neisser and Friedemann: München med. Wochenschr., **51**, 827 (1904); cf. Weiser and Nicholas: J. Phys. Chem., **25**, 743 (1921).

[4] Bechhold: Z. physik. Chem., **48**, 385 (1904).

[5] Odén: Z. physik. Chem., **78**, 682 (1912).

[6] Burton and Bishop: J. Phys. Chem., **24**, 701 (1920).

The purpose of the work presented in this paper was to determine the effect of varying dispersity, of concentration and of variety of mastic on the concentration of potassium chloride required for precipitation of mastic suspensions at varying concentrations of hydrogen-ion. The work of Michaelis and his coworkers had already shown conclusively a reciprocal relation of hydrogen-ion concentration and salt concentration in the precipitation of a given sol. The results of their work render valueless the conclusions of so many papers dealing with precipitation in which the effect of hydrogen-ion concentration has been neglected and also are so far reaching in the development of a more complete knowledge of the precipitation of colloids by electrolytes, that it seemed very necessary that their work be subjected to verification and be extended considerably in its scope. Because of lack of time the work was limited to precipitation with a single electrolyte. The authors believed it better to make a thorough study with one precipitating agent than to use several and be obliged to otherwise limit the extent of the investigation.

Experimental Part

Preparation of Colloids

Twenty per cent solutions in neutral alcohol of two different varieties of gum mastic, one a powdered sample (Merck's) and the other a sample of the tears of the original gum, were allowed to settle until clear. Each sol was prepared in the usual manner by allowing the alcoholic solution to run slowly into water from a burette with a capillary tip which was held under the surface while the mixture was constantly and rapidly stirred. Variation in the degree of dispersity of the sols was sought by regulating the rate of flow of the alcoholic solution into the water; the time required for the flow of one cc. of the alcoholic solution through the capillary tip was varied from 12 to 85 seconds. The suspensions were permitted to stand for at least four weeks. Then the upper portion to within four cm. of the bottom of the container was siphoned off and transferred to well-seasoned bottles for use. Thereafter the sols were always well shaken before sampling. A very little chloroform was added to each sol to inhibit the growth of mold. Later the total concentrations of the mastic in grams per liter was determined by evaporation to constant weight at 105°.

Data descriptive of the different samples of mastic suspensoid employed are given in Table I. Those prepared from Merck's powdered mastic and designated as 1M to 4M inclusive were of a very light cream color. The others marked from 5T to 15T inclusive which were prepared from gum mastic tears, were milky white in color. The Sörensen values (pH) of the different sols have also been included in the table; they will be discussed in a later portion of this paper.

Precipitation with Potassium Chloride alone

In all cases the method of effecting precipitation and the decision as to completeness of precipitation were the same. The precipitating agent diluted with distilled water in a large test tube to 20 cc., was poured rapidly into 20 cc.

TABLE I

Preparation of Mastic Suspensoids

Sol. No.	Mastic per liter (G.)	Alcohol Content per liter of sol (cc.)	Rate of Addition of Alcoholic Mastic (Seconds per cc.)	pH of Sol
1M	5.738	50	30	
2M	3.490	25	85	3.60
3M	3.148	25	77	3.65
4M	2.486	25	30	——
5T	3.074	25	36	4.08
6T	3.026	25	52	——
7T	2.752	25	18	——
8T	2.945	25	12	——
9T	0.783	6.3	46	——
10T	1.562	12.5	50	——
11T	6.317	50	46	3.87
12T	2.352	25	85	3.91
13T	11.406	100	38	3.47
14T	3.048	25	46	3.92
15T		55	46	3.84

of the colloid contained in another tube. After pouring back and forth 6 times to insure complete mixing the mixture was set aside in a thermostat at 25° for 24 hours and then examined. If completeness of coagulation was doubtful because of the non-settling of the mastic coagulum the content of the tube was centrifuged for 15 minutes in an International Centrifuge No. 1 at 2500 r.p.m. When the supernatant liquid after centrifuging appeared very clear and not opalescent, precipitation was deemed complete. After some preliminary tests, the minimal concentration for precipitation was determined from a series of four mixtures of each sol with the precipitating agent in which the concentration of the latter varied from tube to tube by 5 to 8 per cent. Each of these final series was duplicated at least once.

The potassium chloride used for precipitation was prepared from recrystallized C.P. salt except for the precipitation in alkalin solution for which a commercial C.P. product was employed. The water used throughout this investigation was distilled water which in this laboratory, has a specific conductivity of always less than 2×10^{-6} reciprocal ohms.

Hydrogen-ion concentrations of the suspension medium in the presence of the coagulum at the minimal precipitation concentrations were determined electrometrically on larger samples of the mixtures which had stood the usual 24 hours. It was repeatedly demonstrated that it was not necessary to remove the coagulum from the suspension medium by centrifuging before determining the pH. This confims the findings of Michaelis and Hirabayashi[1]. E.M.F.

---

[1] Michaelis and Hirabayashi: Kolloid-Z., **30**, 209 (1922).

measurements were all conducted in an air thermostat at 25°. Two hydrogen electrodes opposed to two different volume normal calomel electrodes with normal potassium chloride bridges were employed in each determination. For those mixtures in which the concentration of potassium chloride was greater than normal, the mixture itself was used in the bridge vessel. Sörensen values were calculated from the formula:

$$\mathrm{pH} = \frac{\text{Observed E.M.F.} - 0.2848}{0.05911}$$

The data from the precipitations with potassium chloride alone are given in Table II. The concentrations are expressed in milliequivalents per liter of the mixture of precipitating agent and sol. For convenience in presenting later the results in graphical form, values are given for the logarithm of the reciprocal of the concentration of potassium chloride in mols per liter, $\log_{10} 1/\mathrm{KCl}$. Dilutions of sols 1M and 11T to two, four and eight times the original volume of the sol, were also precipitated, the dilution indicated in the table being that of the sol before admixture with the precipitating agent.

TABLE II

Potassium Chloride and Hydrogen-Ion Concentrations in the Coagulation of Mastic Suspensoids with Potassium Chloride alone

Sol No.	Dilution of sol before mixing (times original volume)	Potassium Chloride, (milli-equivalents per liter)	$\log_{10} 1/(\mathrm{KCl})$	pH
1M	1	46	1.33	3.54
1M	2	65	1.19	3.75
1M	4	93	1.03	4.01
1M	8	115	0.94	4.23
2M	1	68	1.17	3.77
3M	1	68	1.17	3.77
4M	1	58	1.24	3.72
5T	1	95	1.02	4.31
6T	1	70	1.15	4.11
7T	1	90	1.05	4.19
8T	1	93	1.03	4.23
9T	1	148	0.83	4.82
10T	1	140	0.85	4.55
11T	1	73	1.14	3.99
11T	2	95	1.02	4.25
11T	4	154	0.81	4.51
11T	8	295	0.53	5.00
12T	1	70	1.15	4.13
13T	1	34	1.47	3.58
14T	1	90	1.05	4.33
15T	1	70	1.15	3.95

Variation in the Natural Acidity of Mastic Sols

The data of Table II showed that the mastic sols had different pH values after precipitation even though they had all been treated in the same manner with the neutral, unhydrolyzed salt, potassium chloride. Comparison with the pH values of the sols alone recorded in Table I made it evident that approximately these same differences in the acidity of the sols existed before precipitation as afterward. Because of the low conductivity of the mastic sols when unmixed with electrolyte, the electrometric determinations were not more accurate than to within 0.03 pH.

Not only did the same differences of acidity exist before and after precipitation but the process of precipitation was attended by no great change in acidity. The variation of the pH of three sols was determined both with amounts of salt insufficient and with amounts in excess of that necessary for complete precipitation. To avoid the change of pH involved in dilution, solid potassium chloride was used in each experiment. The data of Table III show that the increase in acidity upon the addition of less than the precipitating concentration of unhydrolyzed salt was less than that equivalent to 0.1 unit of pH. The addition of amounts of potassium chloride larger than necessary for precipitation was accompanied by a further decrease of less than 0.03 units of pH. Although the conductivity of the sol alone was too low to give satisfying accuracy in the determination of the pH of the suspension medium in the absence of salt, there was indicated in each instance a slight but definite increase in acidity, the greatest change occurring upon the addition of the first small amount of potassium chloride. This may have some significance. That there is no marked liberation of hydrogen or hydroxyl ions in the precipitation of suspensoids has likewise been observed by Pauli and Matula[1] and by Browne[2] working with ferric oxide sols.

TABLE III

Change of pH of Mastic Suspensoids upon Addition of Solid KCl

Sol No.	solid KCl per 100 cc. sol (grams)	pH	Sol No.	solid KCl per 100 cc. sol (grams)	pH
3M	0.0	3.65	5T	0.0	4.08
	0.1	3.56		0.1	4.02
	1.0	3.57		0.2	4.03
	1.0	3.56		0.5	4.02
11T	0.0	3.87		1.0	4.03
	0.1	3.83		1.0	4.02
	1.0	3.80		2.0	3.99

---

[1] Pauli and Matula: Kolloid-Z., 21, 49 (1917).

[2] Browne: J. Am. Chem. Soc., 45, 311 (1923).

Because of the great importance of acidity at precipitation, it also became necessary to investigate the differences in the acidity of the different mastic suspensoids and even to learn the source of the acidity in order to gain a more complete knowledge of the conditions governing their precipitation. Observations made from the processes of ultrafiltration and dialysis proved that the hydrogen-ion concentration of a mastic suspensoid is due principally, within the limit of experimental error, to organic acid in true solution in the suspension medium. Four of the sols were slowly ultrafiltered under a hydrostatic head of three meters through a paper extraction thimble which had been heavily treated with collodion and then soaked in distilled water for two days. The ultrafiltrate was clear to the eye and gave only a faint Tyndall beam. Electrometric determinations were made of the hydrogen-ion concentrations; also of the total available hydrogen-ion by titration with dilute sodium hydroxide using phenolphthalein as indicator. The data are recorded in Table IV and show that in each instance the ultrafiltrate does not apparently contain so great a concentration of hydrogen-ions as the sol itself. Such a condition might be expected from the principle of Donnan membrane equilibrium. A comparison of the electrometrically determined hydrogen-ion concentration with the total available hydrogen-ion ascertained by titration indicates that from 11 to 25 per cent of the acid in the ultrafiltrate was ionized. The residue obtained by evaporation showed that approximately 4 per cent of the gum mastic of the mastic suspensoid was in true solution. The equivalent weight[1] of this residue was very roughly about 400. When the residue from the ultrafiltrate was again dissolved in a small amount of alcohol and the solution then poured into water a colloidal suspension was obtained which closely resembled in appearance the original mastic sol.

TABLE IV

Acidity of Ultrafiltrates from Mastic Suspensoids

Sol	pH of sol	pH ultrafiltrate	Hydrogen-ion concentration of ultrafiltrate		Grams residue per liter ultrafiltrate	Equivalent weight of residue
			Electrometric	Total Acidity (titrated)		
5T	4.08	4.48	0.33×10^{-4}	2.0×10^{-4}	0.09	440
11T	3.87	4.06	0.87×10^{-4}	5.3×10^{-4}	0.26	490
14T	3.92	4.06	0.87×10^{-4}	7.6×10^{-4}	0.19	250
15T	3.84	4.11	0.78×10^{-4}	3.0×10^{-4}	0.12	400

An unsuccessful attempt was made to find whether the amount of acid in true solution varied with the alcohol content of the sol. To this end sols 14T and 15T were both made from the same original sol by dilution, sol 14T with pure water and sol 15T with alcohol and water such that the final alcohol content of 15T was more than twice that of 14T. Otherwise these two sols were absolutely identical. The hydrogen-ion concentration was slightly greater in 15T, the one with the greater alcohol content; but in the ultrafiltrate the order was reversed. Either the accuracy of the work was not sufficiently great to bring out any consistent difference, or else, as will be shown later in another manner, the percentage of alcohol within these lower limits is without marked effect on the hydrogen-ion concentration of a mastic sol.

---

[1] Tschirch and Reutter (Arch. Pharm. **242**, 104 (1888); see also Tschirch: "Die Harze und die Hartzbehälter", **1**, 468 (1906)) have found gum mastic to contain: α and β masticic acids ($C_{23}H_{36}O_4$; mol. wt. = 376.3) – 4.0%. Masticolic acid ($C_{23}H_{36}O_4$; mol. wt. = 376.3) – 0.5%. α and β masticonic acids ($C_{32}H_{48}O_4$; mol. wt. = 490.6) – 38.0%. α mastic resin ($C_{35}H_{56}O_4$) – 31.0%. These constituents are soluble in alcohol and the acids are monobasic.

Dialytic experiments also showed that the acidity of the mastic sols was due principally to organic acid (or acids) in true solution. A collodion sack filled with distilled water at room temperature was placed in a liter of mastic sol. The level of water in the sack was kept constant with a constant level siphon. Distilled water flowed freely through a capillary tube into the sack at the rate of 1 liter in twelve hours. The total volume of the dialysate was twenty liters. This arrangement was essentially that employed by Neidle[1] for hot dialysis. The first of the dialysate contained about 16 mg. of dissolved material per liter while the last contained perhaps less than 1.0 mg. per liter. The acidity of the dialysate distinctly decreased during the dialysis as shown with the methyl red indicator. Sol 5T gave an electrometric pH of 4.08 before dialysis but after dialysis the acidity had decreased to a value corresponding to a pH of 5.7. Since the conductivity of the sol largely decreased during dialysis it became increasingly difficult to determine electrometrically the Sörensen value with satisfactory accuracy. However, the values here were checked roughly with indicators. One portion of sol 5T after dialysis was diluted with carefully prepared neutral alcohol and water to an alcohol content of 25 cc. per liter and another portion to an alcohol content of 50 cc. per liter. During the next few days the pH values of the first portion were 4.87, 4.88 and 4.7. A dilution of the original sol itself with an equal volume of water gave a pH value of 4.37. The portion of dialyzed sol diluted with the double quantity of alcohol gave pH values of 4.9, 4.8, and 4.5. These figures show that although the presence of the alcohol distinctly increased the acidity of the dialyzed sol, there was no marked difference between the effects of 2.5% and 5% alcohol. The pH value of sol 11T was determined after dialysis and dilution with an equal volume of water and found to be 5.7. But upon dilution of the dialyzed sol with alcohol and water to an alcohol content of approximately 25 cc. per liter, a pH of 4.7 was obtained. The original sol 11T itself before dialysis gave a pH value of 3.87 while a dilution of two gave a pH value of 4.08.

The effect of dilution of distilled water upon the acidity of the suspensoids was determined. Sols 12T, 13T and 16T were diluted by two, four and eight times the original volumes and the hydrogen-ion concentrations then measured. The data are recorded in Table V.

---

[1] Neidle: J. Am. Chem. Soc., 38, 1270 (1916).

TABLE V

Decrease of Acidity of Mastic Suspensoids with Dilution

Sol	Dilution	Sörensen value (electrometric) pH	Concentration of hydrogen-ion (mols per liter)
12T	1	3.91	12.5×10^{-5}
	2	4.20	6.3
	4	4.49	3.25
	8	4.89	1.3
13T	1	3.47	34.0
	2	3.67	21.5
	4	3.87	13.5
	8	4.10	8.0
16T	1	4.25	5.65
	2	4.43	3.7
	3	4.57	2.7
	4	4.75	1.7
	5	4.85	1.4
	6	5.06	0.87

The decrease in hydrogen-ion concentration, or increase of pH, was nearly proportional to the amount of dilution. The experiments on the precipitation of the diluted sols with potassium chloride (see Table II) also showed nearly the same rate of decrease of hydrogen-ion concentration, namely about 0.25 unit of pH for each halving of the concentration.

Coagulation of Mastic Suspensoids in Acid and Basic Solution with Potassium Chloride

In order to cover a wide range of pH in this work, precipitations were conducted with hydrochloric acid alone, with hydrochloric acid and potassium chloride, and with potassium chloride and potassium hydroxide, using sols which differed widely in concentration and with dilutions of two and four times the volume of one sol of each variety. In these experiments the methods outlined for the precipitations with potassium chloride alone were followed. The data are recorded in Tables VI, VII and VIII. The electrometric determinations of pH were very satisfactory except those conducted in neutral or basic solution the values for which are given in Table VIII. The e.m.f. of the chain in these latter determinations rose rapidly in about ten minutes to a maximum and then decreased. Since the pH indicated by the maximum e.m.f. corresponded to the pH obtained with indicators, it was assumed to be approximately correct. The irregular behaviour of the hydrogen electrode in the pH range beyond 6.0 in solutions which are not well buffered is to be expected according to the timely work of Beans and Hammett[1].

---

[1] Beans and Hammett: J. Am. Chem. Soc., **47**, 1215 (1925).

Table VI

Coagulation of Mastic Suspensoids with Hydrochloric Acid alone

Sol	Dilution of sol before mixing (times original volume)	HCl, milli-equivalents per liter mixture	Hydrogen-ion, milli-equivalents per liter	pH
1M	1	6.60	5.89	2.23
	2	6.60	5.89	2.23
	4	6.49	5.62	2.25
2M	1	8.06	6.76	2.17
5T	1	4.92	4.37	2.36
9T	1	3.77	3.31	2.48
10T	1	4.50	3.98	2.40
11T	1	4.16	3.55	2.45
	2	4.40	3.98	2.40
	4	4.19	3.89	2.41

Table VII

Coagulation of Mastic Suspensoids with Hydrochloric Acid in Addition to Potassium Chloride

Sol	Dilution of sol before mixing (times original volume)	HCl, Milli-equivalents per liter mixture	pH, electrometric	$\text{Log}_{10} \frac{1}{(\text{KCl})}$
1M	1	1.26	2.87	1.70
	2	1.26	2.90	1.70
	4	1.41	2.87	1.70
2M	1	1.62	2.81	1.70
5T	1	6.60	2.25	1.70
9T	1	0.73	3.18	1.70
11T	1	0.63	3.22	1.70
	2	0.73	3.16	1.70
	4	0.84	3.11	1.70
2M	1	3.93	2.43	2.0
	2	3.93	2.44	2.0
11T	1	2.20	2.69	2.0
11T	2	2.41	2.66	2.0

Note: The concentration of potassium chloride in the mixture was 20 milli-equivalents per liter in the one set of experiments and 10 milli-equivalents per liter in the other set of experiments.

TABLE VIII

Coagulation of Mastic Suspensoids with Potassium Chloride and Potassium Hydroxide

Sol	Dilution of sol before mixing (times original volume)	KCl, milli-equivalents per liter mixture	pH, electrometric	$\text{Log}\,\frac{1}{(\text{KCl}+\text{KOH})}$
1M	1	1310		−0.12
	2	1925	7.4	−0.28
	4	2100	7.7	−0.32
2M	1	1575	7.6	−0.20
5T	1	1660	9.7	−0.22
9T	1	1575	10.3	−0.20
11T	1	1490	8.5	−0.17
	2	1400	9.16	−0.15
	4	1400		−0.15

Note: The concentration of potassium hydroxide in the mixture was 0.92 milli-equivalents per liter in each case.

Discussion of Results and Conclusions

The importance emphasized by Michaelis and his coworkers of hydrogen-ion concentration in the study of the precipitation of mastic suspensoids has been more than justified by the results of the experimental work presented in this paper. The data show a reciprocal relation between pH and log 1/(KCl), namely, the greater the hydrogen-ion concentration the less potassium chloride is required for precipitation.

The first purpose of this research was to determine the effect of variation of dispersity, of concentration, and of kind of mastic on coagulation. Of these only the last, the variety of mastic, has a definite influence per se, on precipitation. The dispersity and concentration of the sol apparently affect coagulation only indirectly through their effect on the hydrogen-ion concentration of the sol itself.

The concentration and dispersity of the sol do have an influence upon the acidity of the dispersion medium of the sol. A consideration of the data will bring out that in general the greater the concentration of the suspensoid the greater is the hydrogen-ion concentration of the sol in the absence of added electrolyte. Further, the hydrogen-ion concentration increases with the slowness with which the alcoholic mastic is stirred into water in the preparation of the sol. The actual dispersity of the sols was not quantitatively determined. But undoubtedly the average dispersity of the different samples varied with the rate of formation of the sols. When it is remembered that the acidity of mastic suspensoids is due principally to organic acid in true solution it would be expected that the amount of acid going into true solution would be effected by the amount and rate of addition of alcoholic mastic to water. It might also be expected that the amount of acid in true solution would be greatly increased with increase in the alcohol content. The addition of dilute alcohol was found to largely increase the acidity of a sol from which the alcohol and acid had been previously dialyzed. However, the addition of twice the concentration of alcohol did not have a much greater effect. It should be again emphasized that the concentration of potassium chloride alone required to coagulate any mastic suspensoid varies with the dispersity and concentration of the sol simply because the pH of the dispersion medium is dependent upon the concentration and dispersity, or manner of preparation.

From the work presented above it is evident that any study of the effect of dilution upon the precipitation (with a univalent ion) of mastic which disregards the effect of dilution upon hydrogen-ion concentration, overlooks the chief factor governing the amount of electrolyte required. The decrease of acidity of mastic suspensoids with dilution furnishes a full explanation of the rule of Burton and Bishop[1] that dilution increases the concentration of uni-univalent salt required for precipitation. A more general and clearer statement of the situation would be that a decrease of hydrogen-ion concentration increases the concentration of salt required for coagulation of mastic suspensoids. The results reported herein indicate that the interpretation of the Burton and Bishop rule in its application to the change of concentration of salts furnishing bivalent and trivalent cations required for coagulation should

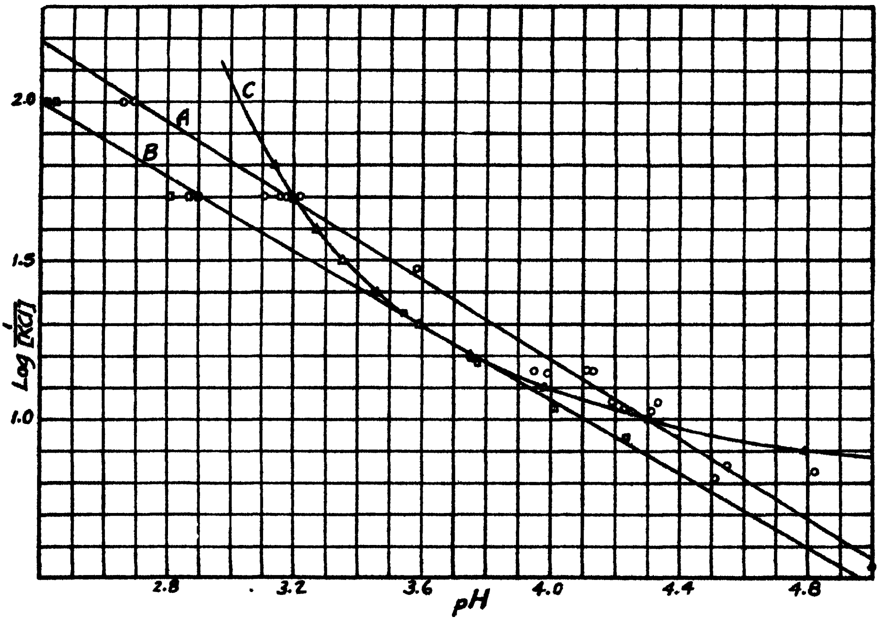


Fig. 1

A—tears mastic; $\log_{10} 1/(KCl) = 3.675 - 0.625$ pH: B—Merck's powdered mastic; $\log_{10} 1/(KCl) = 3.405 - 0.590$ pH: C—Equilateral hyperbola calculated by method of Michaelis and coworkers; $(\log_{10} 1/(KCl) + 0.18)(pH - 2.43) = 2.24$

---

[1] Burton and Bishop: J. Phys. Chem. 24, 701 (1920).

be made only after a consideration of the effects of both dilution of the sol and of hydrolysis of the salt on the hydrogen-ion concentration.

When the values of log 1/(KCl) and pH corresponding to coagulation concentrations of potassium chloride and hydrogen-ion concentrations for all the suspensoids prepared from mastic tears and dilutions of these suspensoids, are plotted as in Fig. 1 it is seen that they all lie approximately on a straight line in the pH range from 3.1 to 5.0. The equation of this line is log 1/(KCl) = 3.675 − 0.625 pH. The values for all the suspensoids and dilutions of suspensoids prepared from Merck's powdered mastic lie on a different line which is nearly parallel and whose equation is, log 1/(KCl) = 3.405 − 0.590 pH for the pH range of 2.4 to 4.3. The effect of variety of mastic on coagulation is clearly shown by these equations. At a given pH a greater concentration of salt is required for the coagulation of the Merck sols. Michaelis[1] and his coworkers expressed the relation between log 1/(KCl) and pH by the hyperbolic equation given in the introduction of this paper. However, they had to explain that for the values near a pH of 4.0 the points lie below the hyperbola. If a straight line is drawn through the middle portion of the Michaelis hyperbola it will be seen that for this portion the "curve" becomes more nearly a straight line (see Fig. 2). It is true that as log 1/(KCl) approaches infinity, that is when precipitations are made with acid alone, the curve becomes asymptotic to an ordinate. Further, when the pH becomes greater than 7.0 the curve as shown by the data of Table VIII, becomes asymptotic to an abscissa. It is believed, however, that for the pH range of 2.4 to 5.0 the re-

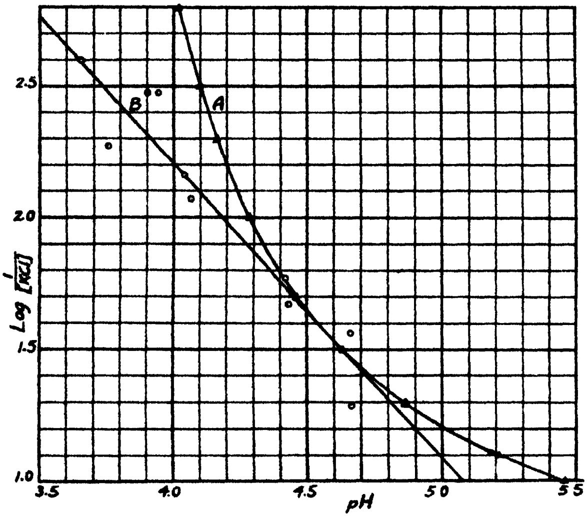


FIG. 2

A—Michaelis' hyperbola, (pH − 3.46) (log 1/(KCl) − 0.3) = 1.4: B—Michaelis and coworkers data for precipitation of mastic with KCl.

---

[1] Michaelis and Timenez-Diaz: Kolloid-Z., 29, 181 (1921); Michaelis and Hirabayashi: 30, 209 (1922).

lation between log 1/(KCl) and pH can better be expressed by the straight line than by the hyperbola drawn in Fig. 1 in the manner employed by Michaelis.

It is unfortunate that there is no universally accepted criterion of complete precipitation. The point of view which governed the adoption of the standard here employed is that there is not definite precipitation unless the coagulum completely flocks leaving the dispersion medium clear. Furthermore, we believe that at least 24 hours is necessary for the attainment, or near attainment, of an equilibrium condition. The change in the appearance of the mixture of sol and precipitant is rapid the first few minutes and even the first few hours. After 24 hours, there is practically no further change apparent. The difference due to varying standards for complete precipitation is well illustrated by the data here in comparison with that of Michaelis and Hirabayashi[1]. The latter workers found precipitation with acid alone at a pH of 2.86. The average pH values at precipitation with acid alone in Table VI is 2.43 for the sols prepared from tears and 2.23 for the Merck sols, the differences from the 2.86 value being greater than can be easily accounted for on an assumption of great differences in kind of mastic.

Summary

1. Mastic suspensoids prepared from different varieties of gum mastic and differing widely in concentration and dispersity are found to possess different hydrogen-ion concentrations and to require different concentrations of potassium chloride for coagulation.

2. The acidity of mastic suspensoids is due principally to organic acid in true solution. The mastic in true solution as free acid can be separated from the sol by dialysis and ultrafiltration. There is no great liberation of hydrogen-ions or hydroxyl-ions during coagulation with potassium chloride. The acidity of a mastic sol decreases with dilution.

3. All the suspensoids of one variety of mastic precipitate at about the same pH with hydrochloric acid alone regardless of the concentration or dispersity. In the pH range beyond 6.0 they all precipitate with nearly the same concentration of potassium chloride.

4. The minimum concentration of potassium chloride for coagulation of a mastic suspensoid is dependent entirely upon the pH of the dispersion medium. When coagulations are conducted at different pH values by varying the acidity of the precipitating agent, the curve relating pH to log 1/(KCl) for minimum coagulation concentrations is shown for one variety of mastic to be the same for the suspensions of different concentration and dispersity. This curve is found to be a straight line, rather than hyperbolic, in the pH range from 2.4 to 5.0. The curves for the suspensoids prepared from two varieties of mastic are not coincident but are nearly parallel.

University of Washington,
Seattle, Washington.
Feb. 20, 1926.

---

[1] Michaelis and Hirabayashi: Kolloid-Z., 30, 209 (1922).

THE ACID-BASIC FUNCTION OF MOLECULES AND ITS DEPENDENCY ON THE ELECTRIC CHARGE TYPE

BY J. N. BRÖNSTED

1. Introduction

The simplest and most adequate definition of acids and bases is given by the scheme[1]

$$A \rightleftarrows B + H^+ \qquad (1)$$

where A and B represent acid and base respectively. This scheme indicates that an acid is defined as a substance, which is able to split off H^+-ions simultaneously forming a base, and a base as a substance capable of uniting with H^+-ions, thus forming an acid.

The unique position of acids and bases among chemical substances is accounted for by the unique properties of the H^+-ion. As the only chemical molecule consisting of an atomic nucleus alone, the hydrogen ion possesses an extraordinary position, particularly an extraordinary mobility, shown by the ease with which it passes from one molecule to another. A similar mobility with any other atom or ion would mean the existence of another group of chemical substances to which the name of acids and bases could be applied with a similar justification.

When the equilibrium given by scheme (1) is established in water or another solvent, the H^+-ion will be solvated. In the case of water as a solvent the equilibrium is [2]

$$A + H_2O \rightleftarrows B + H_3O^+ \qquad (2)$$

which is a double acid-basic equilibrium[3], A and H_3O^+ acting as acids, B and H_2O as bases. The scheme (1) in such a case does not furnish an accurate representation of the *kinetics* of the reaction. It retains, however, unrestricted thermodynamic significance, and its application instead of the more complicated scheme (2) is justified in all cases of non-kinetic nature[4], when the solvent in which the equilibrium takes place remains unchanged.

Application of scheme (1) as a definition of the conception of acids and bases involves the admittance of the acid and basic properties being in principle assignable to ions as well as to neutral molecules. If, for instance, A is acetic acid, B, the base, must be the acetate ion. If B indicates ammonia, A, the acid, must indicate the ammonium ion etc. This is a point of view of considerable consequence. It brings to existence at once the problem of the

---

[*] Contribution from the Physico-Chemical Laboratory of the Polytechnical Institute of Copenhagen.

[1] Brönsted: Rec. Trav. chim., **42**, 718 (1923).

[2] Compare Goldschmidt and Udby: Z. physik. Chem. **60**, 728 (1907); Fajans: "Die Naturwissenschaft," **10**, 165 (1923); Lowry: Trans. Faraday Soc., **20**, Nr. 58 (1924).

[3] Brönsted: l. c. p. 721.

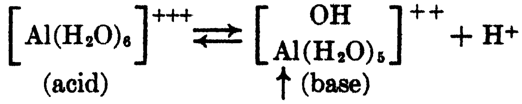
[4] The kinetic significance of the hydration of the H+-ion will be considered in another paper.

influence of the electric charge upon the acid-basic properties of molecules. This problem, in some sense, is not entirely new. When comparing the first and the second dissociation step of a dibasic acid for instance, what actually is compared is the dissociation of an electrically neutral acid and an acid of one negative electric charge. The present definition, however, involves the necessity of a general extension of the point of view from which such special cases[1] have been considered.

2. The Acid Nature of Aquo-ions

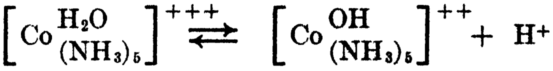
The influence of the total charge of the acid molecule.

When an aluminium salt is dissolved in water the aluminium ion unites with the solvent forming an aquo-ion, probably the hexaquo aluminium ion. This is an acid, dissociating according to:



$$\underset{\text{(acid)}}{\left[\mathrm{Al(H_2O)_6}\right]^{+++}} \rightleftarrows \underset{\uparrow\ \text{(base)}}{\left[\begin{matrix}\mathrm{OH}\\ \mathrm{Al(H_2O)_5}\end{matrix}\right]^{++}} + \mathrm{H^+}$$

and forming the hydroxo-pentaquo-ion as a base. Another acid of a similar type is the aquo-pentammine cobaltic ion, which dissociates according to the scheme:



$$\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O}\\ \mathrm{(NH_3)_5}\end{matrix}\right]^{+++} \rightleftarrows \left[\mathrm{Co}\begin{matrix}\mathrm{OH}\\ \mathrm{(NH_3)_5}\end{matrix}\right]^{++} + \mathrm{H^+}$$

forming as a base the hydroxo pentammine cobaltic ion.

Particularly through the study of the cobaltic ammonia and similar metal ammonia salts, which possess a notable degree of definiteness and stability a certain insight has been obtained into the properties of aquo ions. For a small number of these the acid constant (dissociation constant) is known with a fair accuracy.

Thus for the aquo pentammine cobaltic ion in about 0.01 molal solution the value:

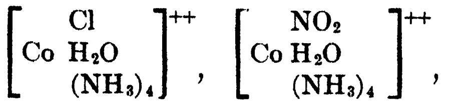
$$K = \frac{\left[\mathrm{Co}\begin{matrix}\mathrm{OH^{++}}\\ \mathrm{(NH_3)_5}\end{matrix}\right]\ [\mathrm{H^+}]}{\left[\mathrm{Co}\begin{matrix}\mathrm{H_2O^{+++}}\\ \mathrm{(NH_3)_5}\end{matrix}\right]\cdot} = 1.10^{-6}$$

has recently been found in this laboratory. When substituting H_2O for one NH_3 the diaquo tetrammine cobaltic ion is formed, possessing an acid constant about three times as great as the constant for the aquo pentammine cobaltic ion. For the triaquo triammine and tetraaquo diammine cobaltic ion the value of the constant is still higher. Part of this increase, however, is accounted for by a statistical effect, which requires for instance a hexaaquo ion to be six times as strong as a monoaquo ion. The acidity, statistically corrected, is therefore not so different as the acid constants ordinarily measured, and the dissociation constant for this type of acids can be considered, at least, of the same order of magnitude.

---

[1] Ostwald: Z. physik. Chem., 9, 558 (1892); Bjerrum: 106, 219 (1923).

If, however, in the aquo-pentammine-cobaltic ion one ammonia group be substituted by an anion as Cl^- or NO_2^- the following ions thus being formed:



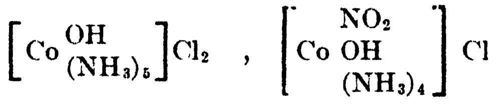
$$\left[\begin{array}{l} \quad Cl \\ Co\ H_2O \\ \quad (NH_3)_4 \end{array}\right]^{++}, \quad \left[\begin{array}{l} \quad NO_2 \\ Co\ H_2O \\ \quad (NH_3)_4 \end{array}\right]^{++},$$

the picture becomes entirely changed. The strength of these acids is not exactly known, but they are at least very much weaker than the above mentioned trivalent ions in which only ammonia and water molecules are combined with the central atom.

The reason for this great difference in acid strength obviously presents itself as the difference in electric charge of the acid molecule. While the aquo pentammine and the other trivalent aquo ions possess three positive charges by which the positive H^+-ions are strongly repelled, the chloro and nitro aquo tetrammine ions contain but two positive charges and accordingly exert a smaller repelling effect. As the process of dissociation in the case of weak acids, even if immeasurably fast from an experimental point of view, still is far from being instantaneous, a small change in the repelling force means a very considerable change in the probability of detachment and taking up of a H^+-ion and so easily accounts for the considerable change in acidity.

As a matter of fact, the electric effect assumed here to be operating as an acidifying factor must be looked upon as an effect of quite general nature. Under otherwise similar conditions a molecule will possess the more acid character the more positive is its electric charge, and the more basic character the more negative it is.

Werner[1], who has studied the basic properties of the various hydroxo salts as for instance

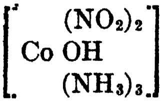


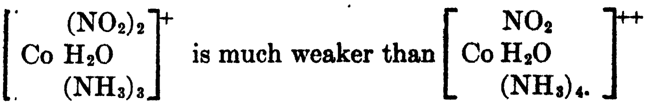
$$\left[Co\begin{array}{l} OH \\ (NH_3)_5 \end{array}\right]Cl_2, \quad \left[\begin{array}{l} \quad NO_2 \\ Co\ OH \\ \quad (NH_3)_4 \end{array}\right]Cl$$

states that the latter of these is much more basic than the former. This, of course, is tantamount to stating that that the $\left[Co\begin{array}{l} H_2O \\ (NH_3)_5 \end{array}\right]Cl_3$ is much more acid than is $\left[\begin{array}{l} \quad NO_2 \\ Co\ H_2O \\ \quad (NH_3)_4 \end{array}\right]Cl_2$. This corresponds entirely to our results. However, Werner does not interpret the phenomenon from the point of view here adduced, and seems rather disposed to find it in contrast to the well known influence of "electronegative" groups when introduced in organic acids. This conclusion, however, may only be justified when considering the salts as not dissociated electrolytically. Werner, certainly, was an adherent to the dissociation theory, but, strange to say, usually states his chemical formulae in undissociated form. He utilizes the dissociation theory mostly for the purpose of elucidating molecular structure. Then, of course, all molecules appear as electrically neutral, and any electric effect as the above mentioned vanishes. Not until writing the salt formulae in correspondance with their electrolytic dissociation is the true nature of the phenomenon disclosed as a simple consequence of the electrostatic forces.[1]

---

[1] Werner: Ber., **40**, 4098, 4117 (1907); "Neuere Anschaungen", 265 (1913).

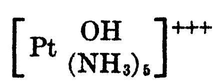
Passing one step further down to acids having only a single positive charge according to the theory presented here, one should expect a still further decrease in acidity. This actually is the case. Dinitrohydroxo triammine cobalt  $\left[\mathrm{Co}\begin{matrix}(NO_2)_2\\ OH\\ (NH_3)_3\end{matrix}\right]$ which is electrically neutral is a much stronger base than the nitro hydroxo tetrammine cobaltic ion, indicating that the corresponding acid:[1]



$$\left[\mathrm{Co}\begin{matrix}(NO_2)_2\\ H_2O\\ (NH_3)_3\end{matrix}\right]^{+} \text{ is much weaker than } \left[\mathrm{Co}\begin{matrix}NO_2\\ H_2O\\ (NH_3)_4.\end{matrix}\right]^{++}$$

In order to test our theory by consideration of ions of still higher positive charge than the aquo pentammine cobaltic ion, in which case a still more pronounced acidity is to be expected, we have to pass on to elements of higher valencies. It is known that platinum in its tetravalent state is able to form a great many complex ions of high stability, and several of these are usable for the demonstration of the applicability of the present point of view.

Tschugajeff[2] has recently discovered a series of salts of the hydroxo pentammine platinic ion:



$$\left[\mathrm{Pt}\begin{matrix}OH\\ (NH_3)_5\end{matrix}\right]^{+++}$$

This, in its composition, is quite analogous to the hydroxo pentammine cobaltic ion, but differs from it in possessing one more positive charge. It is now very remarkable that salts of this ion even of appreciable solubility separate from solutions containing a great excess of hydrochloric acid. From this observation we are justified in concluding that the equilibrium:

$$\underset{\text{(acid)}}{\left[\mathrm{Pt}\begin{matrix}H_2O\\ (NH_3)_5\end{matrix}\right]^{4+}} \rightleftarrows \underset{\text{(base)}}{\left[\mathrm{Pt}\begin{matrix}OH\\ (NH_3)_5\end{matrix}\right]^{3+}} + H^+$$

---

[1] "The strengths of cobaltammine bases" has been the subject of a study by Lamb and Yngve: (J. Am. Chem. Soc., **43**, 2352 (1921)). The bases investigated are, with a single exception, strong, i.e. completely or practically completely dissociating electrolytes. The conductivity method as used by the authors is therefore, unable to give any information about the relative strength of the bases, which are in their character quite different from the weak bases dealt with above.

The conclusion was made by the authors, that the substitution of acid groups for ammonia in the hexammine ion should tend to increase the strength of the corresponding base as a consequence of the diminished positive valence of the ion, is in principle quite in harmony with the general results of the present article. The failure of the measurements to show such an effect is merely due to the inadequacy mentioned of the method in determining the relative strengths of the bases, and is not to be taken in favor of the assumption of a "chemical" influence of the acid radical, offsetting the electric effect, as supposed by the authors.

[2] Tschugajeff: Z. anorg. Chem., **137**, 1 (1924).

is located absolutely in favor of the hydroxo system, i.e. that the tetravalent aquo ion is an acid of a character much like hydrochloric acid or other strong acids, the crucial feature of which actually is their failure to exist. When considered in connection with the properties of analogous ions of lower charge this phenomenon announces in a very remarkable manner the presence of a high positive charge in the acid molecule.

The same distinction between the trivalent cobaltic and the tetravalent platinum ion is exhibited in another way. While the hexammine cobaltic ion $[Co(NH_3)_6]^{+++}$ is practically an absolutely neutral substance, hydrogen ions having no measurable tendency to leave the ammonia molecules, the hexammine platinic ion $[Pt(NH_3)_6]^{4+}$ seems to possess an acid character shown by the fact that salts of this ion are more soluble in alkali than in pure water. This phenomenon must be interpreted by assuming the following equilibrium:

$$[Pt(NH_3)_6]^{4+} \rightleftarrows \left[Pt\begin{matrix}NH_2\\(NH_3)_5\end{matrix}\right]^{3+} + H^+$$

to exist, indicating the ability of the high positive charge to expel a hydrogen ion, even when this forms a part, as it does, of an ammonia molecule of much less acid character than a water molecule.

The acidifying influence of a high positive charge is thus clearly demonstrated by these examples. The acidity of the tetravalent platinic ions, however, seems considerably stronger than one should anticipate from the change in strength exhibited within the group of cobaltic ions. This fact and others let one surmise that the total charge of the molecule is not the only acidifying factor of electrostatic origin, but that also the charge of the central atom of the complex molecule may affect the acidity. The existence of such an effect is actually the basis of the theory of Kossel, which we shall consider in the next chapter.

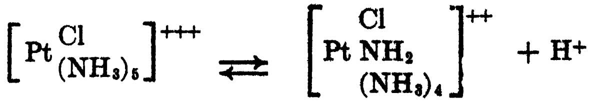
3. The Influence of the Charge of the Central Atom

The great majority of the acids are characterized by a structure more or less similar to that of the aluminum ion or the hexammine cobaltic ion, i.e. an arrangement in which a *central atom* is surrounded by a number of atoms or molecules, which in correspondance with the theory of Werner have a *coordinate* position to it.

In order to show that the effect of the total charge of the molecule is paralleled by an influence of the charge of the central atom, it is necessary to compare ions of the same total charge but with varying charge of the central atom. When for instance comparing the hexammine cobaltic and the chloropentammine platinic ions:

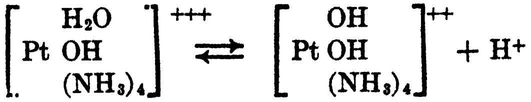
$$\left[Co(NH_3)_6\right]^{+++}, \quad \left[Pt\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right]^{+++}$$

we have in both cases trivalent ions, the central atom, however, possessing in the first case 3 and in the second case 4 positive charges. Now, as mentioned, the cobaltic ion is quite neutral. The platinic ion on the other hand possesses acid character, for adding sodium hydroxide to a solution of the chloride an amido chloride is precipitated[1]:



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\ (\mathrm{NH_3})_5\end{matrix}\right]^{+++} \rightleftarrows \left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\ \mathrm{NH_2}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{++} + \mathrm{H^+}$$

The same influence of the charge of the central atom exists in the case of aquo ions. The non-basic nature of the hydroxo ions of the platinic series is not only characteristic of the hydroxo-aquo-tetrammine ion as shown by Werner[2], both these ions being trivalent, but also the bivalent dihydroxo tetrammine platinic ion is almost non-basic, as shown by the fact that the corresponding salts are not transformed by strong acids into aquo salts. The chloride only adds one molecule of hydrochloric acid, but this is so loosely bound that it disengages even on exposing the solid salt to the air. Therefore the equilibrium:



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{H_2O}\\ \mathrm{OH}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{+++} \rightleftarrows \left[\mathrm{Pt}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ (\mathrm{NH_3})_4\end{matrix}\right]^{++} + \mathrm{H^+}$$

is located almost absolutely in favor of the right-hand system, showing the great strength of the aquo ion in spite of its total charge being only three.

The point of view here stated of the charge of the central atom as an origin of acidity has, as mentioned above, already been advanced in the elaborate and important theory of Kossel[3]. According to this theory the acidity of such molecules as HCl, H_2O and H_3N is determined by the different negative charges: 1, 2 and 3 respectively of the atoms holding the H^+-ion. The weak attraction between H^+ and a singly charged Cl^--ion allows the H^+ to escape easily from the HCl molecule thus making it a strong acid, while the double charge of the O-atom and still more the triple charge of the N-atom prevent the H^+ from ionizing to any appreciable extent. Similarly the positive charge of a central atom to which a water molecule, a hydroxyl group, etc., is bound at the same time as it holds the negative atom of such a group by electric attraction tends to disengage the positive H^+-ion. On that account perchloric and sulphuric acid and other acids with a central atom of high positive charge are strong acids.

The conclusions of Kossel here exemplified only by a few instances rest upon a fundamental assumption, that the various atoms within the structure of the molecule are still free to exert attracting and repelling forces as a direct consequence of their ionic charges. This standpoint may be open to some modification. Fajans[4] has pointed out the great influence of the electric deformation of molecules, a factor undoubtedly of importance but not as yet very well defined. In spite of such criticism, for an orientation in the theory of the origin of acidity the Kossel view points are undoubtedly of great value.

---

[1] Tschugajeff: Z. anorg. Chem., **137**, 401 (1924).

[2] Ber., **40**, 4093 (1907).

[3] W. Kossel: Ann. Physik, (4) **49**, 229 (1916).

[4] Fajans: "Die Naturwissenschaften," **10**, 165 (1923).

It would seem natural to try to work up generally the Kossel theory with the point of view of the present article on the acid-basic function of molecules. Considering the different groups of periodic table we must expect each ion with its natural positive charge, i.e. the charge corresponding to the electronic configuration of the next lower rare gas, to combine, when dissolved in water, with water molecules, thereupon loosing a number of H^+-ions, increasing with the number of positive charges in the series of elements considered. The outcome of such a process is most clearly illustrated by considering a special group for instance the second group of elements ranging from neon to chlorine. The behaviour of these elements is shown in the following scheme, where the figures at the tops of the columns indicate the natural positive charge of the element below, and the figures under the formulae of the various molecules the corresponding charge. In stating the formulae no special consideration has been given to the problem of the degree of hydration.

1	2	3	4	5	6	7
—	—	—	SiO_4 −4	PO_4 −3	SO_4 −2	ClO_4 −1
—	—	—	$HSiO_4$ −3	HPO_4 −2	HSO_4 −1	—
— —	— —	AlO_3 −3	H_2SiO_4 −2	H_2PO_4 −1	H_2SO_4 0	—
— —	— —	$HAlO_3$ −2	H_3SiO_4 −1	H_3PO_4 0	—	—
—	—	H_2AlO_3 −1	H_4SiO_4 0	—	—	—
—	—	H_3AlO_3 0	—	—	—	—
—	—	H_4AlO_3 +1	—	—	—	—
—	H_3MgO_2 +1	H_5AlO_3 +2	—	—	—	—
H_2NaO +1	H_4MgO_2 +2	H_6AlO_3 +3	—	—	—	—

When a positive chlorine ion Cl^{7+} dissolves in water, it forms a hydrate say $Cl(H_2O)_4{}^{7+}$ and then loses eight H^+-ions. The repelling forces of the positive central atom are so strong that even the last of the 8 H^+-ions, after the molecule $HClO_4$ has been formed, leaves the molecule completely. The ion ClO_4^-, therefore, is the only form in which the Cl^{7+} ion can exist in aqueous solution.

A sulphur ion S^{6+} behaves similarly, has a great tendency to losing eight H^+-ions thus forming SO_4^{--}. The smaller charge in comparison with the Cl^{7+}-ion, however, is indicated by the existence of HSO_4^- and possibly also in very slight concentration: H_2SO_4. In these molecules only seven and six H^+-ions respectively are lost.

A phosphorus ion P^{5+} has a still smaller tendency to lose H^+-ions. Eight H^+-ions are lost only in a solution containing great excess of a strong base. Dissolved in water at ordinary concentration the P^{5+}-ion gives rise to formation of HPO_4^{--}, $H_2PO_4^-$ and H_3PO_4 molecules, corresponding to a disengagement of 7, 6 and 5 H^+-ions respectively.

In the case of the Si^{4+} ion the force expelling the H^+-ions from the hydrated ion has decreased so far that the molecule H_4SiO_4 corresponding to a loss of four H^+-ions is the stable form under ordinary conditions. Only in the presence of a large excess of alkali are more H^+-ions split off and ions of negative charges formed.

A still more marked change in acid character is shown by the trivalent aluminum ion Al^{3+}. Under normal conditions this ion loses no or only one H^+-ion. On the other hand, in basic solution it may be brought to lose up to six H^+-ions forming as the most negatively charged molecule the aluminate ion AlO_3^{3-}. In spite of its lower positive charge than that of the previous atoms aluminum is the first element in this series to exist in aquous solution with a positive charge. However, this property does not show up suddenly as quite a novel property, but merely indicates a further step in the graduation of acidity.

By the magnesium ion Mg^{2+} a further alteration in the same direction is exhibited. When dissolved in water the hydrated ion shows no appreciable tendency to losing H^+-ions. Undoubtedly, however, the magnesium ion possesses a weak acid character, as shown particularly at higher temperatures, and we must believe that an ion as $MgOH^-$ or $H_3MgO_2^-$ is capable of existence[1].

Finally the sodium ion in aqueous solution seems completely neutral, i.e. the number of H^+-ions disengaged by it is zero. One should expect even in this case an increase of acidity of the H_2O-molecule by combining with a singly charged positive ion. This increase seems, however, in the case of sodium too small to be demonstrated experimentally[2].

A clear picture of the dependency between acidity and electric charge in this series of elements is given in Fig. 1. Here the natural positive charge of the ions is used as an abscissa. The ordinate indicates the number of H^+-ions lost by each ion, when transferred from a free state into an aquous solution in which the H^+-ion concentration is kept at the value 10^{-7}. The ordinate 6.5 f. instance belonging to P thus indicates a loss of 6.5 H^+-ions by one P^{5+}-ion, i.e. a state of the dissolved P^{5+}-ion corresponding to a mixture of HPO_4^{--} and $H_2PO_4^-$ in equal proportions. This mixture is known to possess a pH value of 7. The ordinate 1 belonging to aluminum indicates this ion to exist at pH = 7 preferably as a bivalent positive ion. The composition of this is known to be $H_{11}AlO_6^{2+}$ or $\left[Al \begin{matrix} OH \\ (H_2O)_5 \end{matrix} \right]^{2+}$.

---

[1] See Gjaldbaek: Z. anorgan. Chem, **144**, 000 (1925).

[2] Bjerrum states (private communication) that he has found some facts that indicate strong solutions of sodium salts to be more acid than corresponding solutions of potassium salts. This agrees excellently with the graduation in acidity to be expected in the series Li-Na-K.

All points, as shown by the figure, can be combined by a smooth curve showing the gradual and continuous change in acidity when passing from an element such as sodium of quite metallic character to metalloid elements as sulphur and chlorine, the acidity thus proving to be a definite function of its natural electric charge.

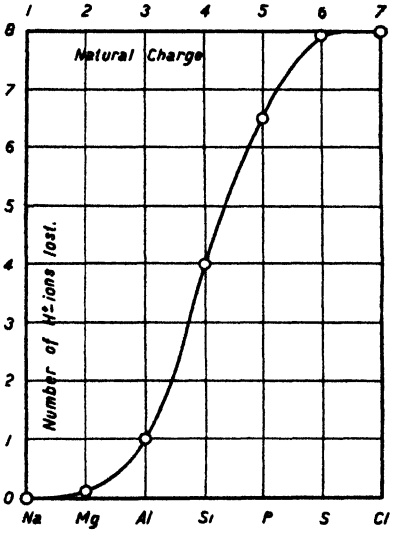


FIG. 1

Besides the magnitude of the electric charge of the central atom also the distance between it and the H^+-atoms plays a part, as already shown by Kossel. When comparing the first series in the periodic table:

Li	Be	B	C	N

with the second

Na	Mg	Al	Si	P

the elements in the first series in correspondance with their smaller atomic volume are found to form hydrated ions of much higher acidity than the elements in the second. Even the lithium ion is certainly not neutral, but possesses a definite acidity[1] and this in the case of glucinum is known to be very pronounced.

---

[1] LiCl shows for instance a tendency to lose HCl in contact with water at a higher temperature. Compare Kolthoff (Rec. Trav. chim., **42**, 969 (1923)) who has attempted to determine the "hydrolysis" of a lithium salt solution.

4. The Influence of the Solvent upon the Acid-Basic Properties

The solvent influences the acid-basic equilibrium in two different ways. 1. Through its dielectric constant. 2. Through its acid-basic properties. We shall consider the last mentioned factor first.

It was stated already in the introduction that the scheme of dissociation of an acid, on account of the hydration of the H^+-ion is somewhat more complex than corresponding to (1) and must properly be represented by:

$$\underset{(\text{acid})_1}{A} + \underset{(\text{base})_2}{H_2O} \rightleftarrows \underset{(\text{base})_1}{B} + \underset{(\text{acid})_2}{H_3O^+}$$

i.e. the scheme of a double acid-basic equilibrium. In fact the H^+-ion or proton has no possibility of existing in the presence of other molecules. In the case of water as a solvent this is illustrated by the extremely high heat of hydration[1] showing its practical non-existence in solution.

The "dissociation" of an acid, therefore, is indespensably connected with the presence of a basic molecule, capable of taking up the H^+-ion expelled[2]. On the other hand a base will undergo no "ionization", i.e. it will add no hydrogen ions unless an acid molecule is present to provide the hydrogen ion required. In order to cause acid and basic "ionization" to occur the solvent thus evidently must possess basic and acid properties itself.

Accordingly for instance in the case of acetic acid, EH, the process of "dissociation" is actually represented by:

$$EH + H_2O \rightleftarrows E^- + H_3O^+ \qquad (3)$$

Putting:

$$\frac{a_{E^-}\, a_{H^+}}{a_{EH}} = K_{EH(a)}$$

and:

$$\frac{a_{H_3O^+}}{a_{H_2O}\, a_{H^+}} = K_{H_2O(b)}$$

where a is the activity, $K_{EH(a)}$ and $K_{H_2O(b)}$ indicate the acid constant of EH and basic constant of H_2O respectively. The tendency of acetic acid to ionize in aquous solution according to scheme (3) therefore is given by:

$$\frac{a_{E^-}\, a_{H_3O^+}}{a_{EH}\, a_{H_2O}} = K_{EH(a)}\, K_{H_2O(b)}$$

i.e. by the product of the two acid and basic constants involved in the reaction. Of course the same product measures the tendency of water to ionize in the presence of acetic acid, these two tendencies being actually identical.

Correspondingly in the case of ammonia in water solution the equation:

$$\frac{a_{NH_4^+}\, a_{OH^-}}{a_{NH_3}\, a_{H_2O}} = K_{NH_3(b)}\, K_{H_2O(a)}$$

where the terms have an analoguous significance, gives the tendency for ammonia and water to ionize in the presence of one another. For the solvent itself a similar equilibrium exists:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

---

[1] Fajans: Ber., 21, 709 (1919).

[2] Compare Lowry: l. c.

showing that the "dissociation" of water is actually an amphoteric reaction one molecule of H_2O acting as an acid and another as a base. Putting:

$$\frac{a_{OH^-}\ a_{H^+}}{a_{H_2O}} = K_{H_2O(a)}$$

and:

$$\frac{a_{H_3O^+}}{a_{H^+}\ a_{H_2O}} = K_{H_2O(b)}$$

the ionization of water is seen to be determined by the constant:

$$\frac{a_{H_3O^+}\ a_{OH^-}}{a^2_{H_2O}} = K_{H_2O(a)}\ K_{H_2O(b)}$$

the product of acid and basic constant thus also in the case of a pure solvent being the factor which determines the ionization.

The widespread opinion that water is equally acid and basic—and therefore quite a neutral substance—thus has to be abandoned. As a matter of fact such a conclusion is by no means justified even if we acknowledge that the ionization of a pure substance is to the same degree depending on its acidity and basicity.

The points of view here presented for the acid-basic function in general, may be useful to explain phenomena, which have not as yet been understood. Thus it is well known that pure substances as a rule are poor conductors for electricity, in other words are but little ionized. This for instance is the case with pure HCl, H_2O and H_3N in a liquid state. Mixtures of these substances, however, may be excellent conductors. How is this phenomenon to be accounted for?

According to the above views ionization in the three cases must occur according to:

$$2HCl \rightleftarrows H_2Cl^+ + Cl^-$$
$$2H_2O \rightleftarrows H_3O^+ + OH^-$$
$$2H_3N \rightleftarrows H_4N^+ + NH_2^-$$

depending upon the values of the three constants:

$$K_{HCl(a)}\quad K_{HCl(b)}$$
$$K_{H_2O(a)}\quad K_{H_2O(b)}$$
$$K_{H_3N(a)}\quad K_{H_3N(b)}$$

Now it is not unreasonable to expect that, as the acid constants in the series HCl, H_2O, H_3N decreases from HCl to NH_3 the basic constants will increase correspondingly in the same direction. It is possible, therefore, that the products are approximately equal. That the conductivity of the three substances in a pure state are of the same order of magnitude, as a matter of fact, shows this conclusion to be justified.

If now mixing for instance HCl and H_2O, the equilibrium:

$$\underset{(\text{acid})_1}{HCl} + \underset{(\text{base})_2}{H_2O} \rightleftarrows \underset{(\text{acid})_2}{H_3O^+} + \underset{(\text{base})_1}{Cl^-}$$

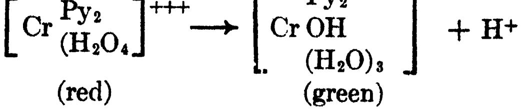
being established, the tendency of the stronger acid HCl to dissociate becomes enhanced by the presence of the stronger base H_2O instead of the very weak base HCl in pure HCl. The ionization as measured by the product $K_{HCl(a)}\ K_{H_2O(b)}$ takes place therefore in the mixture at a much greater extent than in the pure solvent. The reaction can also be considered from the point of view that the tendency of the H_2O-molecule to act as a base, i.e. to unite with a H^+-ion is greatly favored by the presence of the stronger acid HCl instead of H_2O and therefore the ionization stronger than in pure water. In quite a similar way the reason for a mixture of H_2O and NH_3 to ionize much more than the pure liquids is seen to be the greater value of the product $K_{(a)}\ K_{(b)}$ in the mixture than in any of the pure solvents.

The second factor determining the ionization values is the dielectric constant of the solvent. It is generally recognized that the ionization of acids and bases increases with increasing dielectric constant of the solvent. This is owing to the diminishing in the electric attraction forces between the ions. It is evident, however, that the conclusion applies only to acids and bases which are negatively charged or electrically neutral. When comparing the following series of acid-basic equilibria:

$$\begin{array}{lll} A^{\circ} & \rightleftharpoons & B^{-} + H^{+} \\ A^{+} & \rightleftharpoons & B^{\circ} + H^{+} \\ A^{++} & \rightleftharpoons & B^{+} + H^{+} \\ A^{+++} & \rightleftharpoons & B^{++} + H^{+} \end{array}$$

it is noticed immediately that only the first is affected, by changing solvent in correspondence with the usual point of view. The second is not affected And the following are affected in the opposite direction. The more positive the acid molecule is, the more is its acid character enhanced by decrease in dielectric constant.

Several experimental observations are in agreement with this conclusion. As examples may be mentioned the dissociation of trivalent aquo ions the dissociation of which increases in aqueous solution by addition of alcohol. A ferric perchlorate solution which is made colorless by an excess of perchloric acid becomes decidedly brown by adding alcohol. A violet solution of chromium nitrate or perchlorate turns green and a red solution of dipyridin tetraquo chromic chloride also green on a similar treatment. In all cases the color change accompanying the change in the medium is caused by the transformation of the trivalent aquo ion into a bivalent hydroxo ion for instance:



$$\underset{\text{(red)}}{\left[\mathrm{Cr}\,\begin{matrix}\mathrm{Py}_2\\(\mathrm{H_2O_4}\end{matrix}\right]^{+++}} \longrightarrow \underset{\text{(green)}}{\left[\begin{matrix}\mathrm{Py}_2\\\mathrm{Cr\,OH}\\(\mathrm{H_2O})_3\end{matrix}\right]^{++}} + H^{+}$$

Dilution with water of course has an effect in the same direction, but the effect of alcohol, acetone, and other organic liquids is much stronger. The several influencing factors are simultaneously operating in any real case and the acid-basic and the other solvation effects may be of influence besides the dielectric effect. However, alcohol is a weaker base than water, and we must consider, therefore, the dielectric effect to be predominating in causing the phenomenon here mentioned.

These results reached by means of theoretical and experimental evidence entails another law as its actual basis: Namely, that under conditions otherwise alike the chemical potential of an ion is higher in a medium of low than in a medium of high dielectric constant, and that this effect is the more marked the higher the valence is of the ion considered. This agrees with the electrostatic theory of the potential of charged particles and with a number of experimental facts for instance that electrolytically dissociating salts are appreciably soluble only in the solvents of high dielectric constant.

When comparing the strength of two acids or two bases consideration of the factors described above is quite obligatory. Comparison, therefore, should be made only when the acids or bases are present in the same solvent. There remain then still solvation effects which are different for the different molecules, and acid and basic constants found experimentally therefore always refer to the acid or base in its solvated state. An absolute comparison of acidity and basicity of definite molecules evidently requires the absence of any solvent medium, including the pure acid or basic liquids themselves.

Accordingly also methods depending upon static or kinetic behavior of acids or bases in the pure liquid state, as for instance those recently proposed by Hantzsch[1], are inadequate to express a definite measure of acid or basic properties of molecules.

Summary

1. The definition of acids and bases by means of the scheme:

$$\underset{\text{(acid)}}{A} \rightleftarrows \underset{\text{(base)}}{B} + H^+$$

involves the admission of ions as well as electrically neutral molecules as acids and bases.

2. The positive electric aquo ions, for instance $Al(H_2O)_6^{+++}$, are acids. The acid property is the more pronounced, the higher the positive charge. The corresponding hydroxions are bases.

3. In correspondence with the theory of Kossel the charge of the central atom of a molecular configuration plays a very great part in imparting to it acid and basic properties.

4. The acidity and basicity of the various molecules formed by the elements in any group of the periodic table show a graduate change in correspondance with the statements in 1., 2. and 3.

5. The electrostatic effect tends to make acids with two or more positive charges more strongly ionizing in solvents of low dielectric constant than in water.

---

[1] Hantzsch: Z. Elektrochem., **29**, 221 (1923); **30**, 194 (1924).

6. The free H^+-ion does not exist. Ionization of acids and bases takes place as a double acid-basic equilibrium involving the solvent molecules. The ionization tendency is measured by the product of an acid and basic constant. This accounts for the slight ionization in pure solvents as HCl or H_2O and the strong ionization in mixture: HCl + H_2O.

7. Absolute comparison of the strengths of two acids or two bases is impossible because it requires the absence of any solvent medium.

Copenhagen,
Denmark,
Dec. 11, 1925.

INTERFACIAL TENSIONS BETWEEN ORGANIC LIQUIDS AND WATER OR AQUEOUS SOLUTIONS

BY JAMES ROBERT POUND

In this paper the author records the measurements of the interfacial tensions at 30° between certain organic liquids, which for brevity are frequently called 'oils', and water or aqueous solutions. The capillary tube method was used, as described by Reynolds[1], and as used by the author in 1922[2]. Some references to the author's previous work will be made below. The aim of the present work was to improve this method of determining interfacial tensions by measuring the densities of the two mutually saturated liquids as well as those of the original liquids, and also to investigate the changes of interfacial tension due to increasing purity of the liquids used and to chemical action between the liquids in contact. For the last purpose the interfacial tensions, and their changes with time, have been observed between certain esters and aqueous solutions.

The determinations of the interfacial tensions were made in the apparatus previously described, i.e. for one apparatus

$$I = k.(d - d') \,.\, (h + r/3\mu), \qquad (1)$$

where k is a constant for that apparatus,

d and d′ are the densities (C.G.S. units) of the two liquids,

h is the difference between the levels of the two interfaces or menisci, the one in and the other out of the capillary tube in the scale divisions of the outer tube,

r is the radius of the capillary tube in centimeters,

μ is the value of one scale division of the outer tube in cm.,

and I is the interfacial tension, I.T., in dynes per centimetre. For the one apparatus $r/3\mu$ is a constant, which too is small compared to h.

The water or aqueous solution used was prepared largely air-free; the water by boiling and cooling, and the solution by exhausting the air from the stock bottle for some time before using; otherwise bubbles of air may come out of the solution after keeping some time in the thermostat at 30° and get into the capillary tube and spoil the experiment. The water or aqueous solution being in place, the oil was introduced from the top or the bottom depending on whether it was the lighter or denser liquid, allowed to attain the thermostat temperature, and then introduced round and into the capillary tube by running out the water or aqueous solution. From the time of the first setting, the two menisci, or interfaces between the liquids, were under observation for hours; several readings being taken in each of several settings. The densities of the two liquids were often determined at the finish of an interfacial tension experiment; the lower liquid was run out directly into the S.G.

---

[1] J. Chem. Soc., **119**, 469 (1921).

[2] Pound: J. Chem. Soc., **123**, 578 (1923).

bottle, and the upper liquid into a separating funnel and thence into the S.G. bottle. All densities, given in C.G.S. units, were determined at 30° in the thermostat and with the usual precautions. The densities of the pure liquids, Table I, are accurate to within a unit or two in the fifth decimal place; those of the liquids from the I.T. tests, Table V, may be considered correct to the fourth decimal place.

At 15° the hydrochloric acid solution was 1.030 Normal, the sulphuric acid solution was 2.796 Normal, and the sodium hydroxide solution was 1.024 Normal. The last solution was freshly made from the best material, but no special precautions were taken to ensure its being carbonate-free. The sodium chloride solutions were nearly saturated and were made as required.

The interfacial tensions, etc., are summarised in Tables I-IV. Each organic liquid or oil used is mentioned in Table I and is there definitely numbered. Where there were used more than one sample of such from *entirely different sources*, these are distinguished by dashes after the number, e.g. the turpentines 5 and 5′. But where there were used different preparations or distillates from the one source, these samples are distinguished by letters after the number, e.g. the turpentine 5 and the distilled turpentine 5a. The interfacial tension experiments between the oils and water are referred to afterwards by these numbers. The I.T. experiments between the oils and the hydrochloric acid solution are numbered as above followed by X; those with the sulphuric acid solution by Y; those with sodium hydroxide solution by Z; and those with the sodium chloride solutions by S. Thus experiment 25aS is the I.T. experiment with the fraction 25a from the distillation of the ethyl acetate 25 and a solution of sodium chloride. It will be convenient, too, to let I = the I.T. between an oil and water, x = the I.T. between it and the hydrochloric acid solution, y = the I.T. between it and the sulphuric acid, z = the I.T. between it and the sodium hydroxide, and s = the I.T. between it and the salt solution.

Table V summarises the density determinations carried out with the mutually saturated liquids. For the first eleven pairs of liquids of the table, the oil and the water were placed overnight in a stoppered flask in the thermostat, and in the morning the two layers were separated and their densities determined. The remaining pairs of liquids were taken directly from the I.T. apparatus. The densities of the original liquids may be obtained from Table I. The mutual solubility of two liquids should cause a decrease in the difference between their densities; for solution of the denser liquid in the lighter will, in general, raise the density of the latter, and solution of the lighter liquid in the denser will lower the density of the denser, and so $(d - d')$ will decrease. The Table V indicates that these normal cases are twice as numerous as the abnormal cases; in the latter the oil is a complex mixture or chemical action occurs between the two liquids. Also the oils dissolve water from the dilute acid and alkali solutions as from pure water, with similar density changes in the oil in these cases; from the sodium hydroxide solution the oils dissolve somewhat less water and the density changes in them are then somewhat less. Also the oils dissolve similarly in water and in dilute acid and

TABLE I

Interfacial Tensions of Liquids against Water at 30°, with their Densities, Boiling-points etc.

No.	Liquid	B. P.	Density 30°/4°	Initial I. T. γ	Interfacial tension (dynes/cm.) Over hrs.	Final I. T.	After hrs.
1a	Petrol	51.5– 78.0°	0.6669	41.6	2	45.0 *	23
1b	Petrol	80.0–100.5	0.70995	40.65	½	43.85*	20
1c	Petrol	101.5–125.5	0.73178	37.50	½	43.3 *	20
1d	Petrol	83–100	0.7102	45.48	2	43.5 *	96
1′	Petrol	97–124	0.72715	46.10	2	46.3 *	96
2	Benzene	80.03–80.13	0.86704	33.10*	20	—	—
3a	Toluene	110.6–110.7	0.85122	33.50	½	34.40*	22
3b	Toluene	110.8	0.85172	34.24*	20	—	—
4a	Xylene	138.6–139.3	0.84844	34.75	24	—	—
4b	Xylene	139.4–139.5	0.85000	36.40	24	—	—
5	Turpentine	——	0.91207	9.84	5	10.3	22
5a	Turpentine	161.5–173.5	0.86614	16.61	1	16.56	20
5′	Turpentine	——	0.85268	11.07	1	10.2 *	46
6	Terebene	——	0.85438	10.45	1	14.24	23
6a	Terebene	174.5–181.5	0.84040	21.70	¼	26.0	22
7	Limonene	75–85°(25mm)	0.91151	2.84	½	1.4	21
8	Pine Oil	——	0.92263	10.88	1	11.20*	64
9	Eucalyptus Oil	——	0.90533	16.24	1½	16.1	20
10	Cineol	——	0.91145	9.0	1	6.6	20
11	Isobutyl alcohol	107.2–107.6	0.79452	(1.5)	—	—	—
12a	Amyl alcohol	130.7–131.6	0.80432	4.97	1	4.05*	20
12b	Amyl alcohol	131.6–132.0	0.80364	4.95	1	4.11*	20
12′a	Amyl alcohol	129.4–130.7	0.8053	4.87	1	4.15*	21
12′b	Amyl alcohol	130.8–131.7	0.8036	4.83	1	3.82*	21
13	Phenyl-ethyl alcohol	218.4–219.2	1.01103	4.51	1	4.60*	25
14	Acetophenone	201.4–201.6	1.01952	12.00	4	12.08*	24
15	Furfural	160.2–161.2	1.14842	5.13	26	—	—
16	Benzaldehyde	179.3–182.0°	1.03784	14.18	48	—	—
16′	Benzaldehyde	178.5–181.5	1.03790	13.99	4	14.18	48
17	Acetic anhydride	137.0–139.8	1.06713	3.1^{z}	—	0	½
17′	Acetic anhydride	137.6–140.0	1.06722	3.7^{z}	—	0	½
18	Quinoline	$(237.5)^{v}$	1.08677	2.87	1½	—	—
19	Aniline	184.1–184.6	1.01298	6.00	½	5.69*	28
20	Chloroform	61.1	1.4688	31.37	19	—	—
21	Carbon tetrachloride	76.5– 76.6	1.57426	42.76*	21	—	—
22	Nitrobenzene	$(210–211)^{v}$	1.19219	24.10	10	23.90*	18
23a	Chlorobenzene	131.5–131.7	1.09304	35.50	2	35.95*	22
23b	Chlorobenzene	131.9	1.09548	35.52	1	37.15*	23
24a	Benzyl chloride	174.0–174.8	1.08699	29.99	5	28.6	20
24b	Benzyl chloride	175.2–178.3	1.08815	30.07	5	27.1	98

TABLE I (continued)

No.	Liquid	B. P.	Density 30°/4°	Interfacial tension (dynes/cm.)			
				Initial I. T. γ	Over hrs.	Final I. T.	After hrs.
25	Ethyl acetate	——	0.88651	6.19	5	5.96*	21
25a	Ethyl acetate	76.8– 77.1	0.88781	6.79	2	6.06*	21
25b	Ethyl acetate	77.1– 77.3	0.88834	6.39	4	6.05*	49
26a	Butyl acetate	120.2–122.2	0.85746	7.46	1	6.78*	21
26b	Butyl acetate	122.2–124.7	0.86057	8.10	2	7.96*	140
26c	Butyl acetate	124.7–127.2	0.86668	11.07	2	10.6 *	67
27a	Amyl acetate	139.0–140.3	0.8545	10.88	3	10.67*	21
27b	Amyl acetate	140.3–142.0	0.85856	12.05	4	12.04*	27
28a	Ethyl butyrate	104.5–107.5	0.87577	12.45	1	12.35*	50
28b	Ethyl butyrate	107.5–112.0	0.87425	13.54	50	13.33*	50
28c	Ethyl butyrate	112.5–117.4	0.87301	13.70	½	13.56*	24
28d	Ethyl butyrate	117.4–123.5	0.87209	14.80	2	14.75*	24
29	Amyl butyrate	——	0.85703	17.70	2½	17.50*	20
29a	Amyl butyrate	166.0–172.5	0.85593	16.80	2½	17.02*	48
29b	Amyl butyrate	172.5–176.6	0.85778	20.78	21	20.57*	48
29c	Amyl butyrate	176.6–183.6	0.85838	22.04	20	21.92*	20
30	Amyl valerianate	——	0.86145	17.80	20	17.94*	20
30a	Amyl valerianate	171.5–178.5	0.85790	16.23	5	16.46*	23
30b	Amyl valerianate	178.5–184.0	0.86042	19.52	2	19.70*	67
30c	Amyl valerianate	184.0–188.5	0.86202	21.15	67	21.10*	67
31a	"Oenanthic ether"	(222–231)[v]	0.85912	19.55	20	19.41*	20
31b	"Oenanthic ether"	(231–240)[v]	0.85912	19.93	20	20.02*	20
32a	Benzyl acetate	214.0–214.9	1.04677	15.41	2	15.10*	50
32b	Benzyl acetate	214.9–215.3	1.04692	15.40	2	15.15*	50
33	Methyl benzoate	197.2–198.0	1.07845	16.63	1	16.91*	65
34	Isobutyl benzoate	240.3–240.5	0.98959	(24.1)	—	—	—
35	Benzyl benzoate	——	1.10851	25.68	2	21.70*	74
35a	Benzyl benzoate	317.8–319.6	1.10797	25.41	5	23.82*	91
36	Methyl salicylate	220.6–221.9	1.17382	22.03	21	22.3	23
37	Amyl salicylate	——	1.04225	29.98	4	29.83*	47
38	Ethyl phthalate	226°(120mm)	1.11051	14.64	2	14.68*	47
39	Ethyl acetoacetate	180.8–182.8	1.01418	3.75[z]	—	2.9 *	48
39′	Ethylacetoacetate	181.4–185	1.01585	3.50[z]	—	3.2 *	26
40	Maize Oil	——	0.9141	5.8	¼	0	8
40a	Maize Oil	——	0.91446	8.95	¼	0	18
40′	Maize Oil	——	0.91136	20.7	¼	19.2	18
41	Cotton-seed Oil	——	0.91107	22.4	¼	20.8	24
42	Sperm Oil	——	0.91407	5.7	¼	3.6	24
42a	Sperm Oil	——	0.91424	3.9	¼	2.7	18

* The density changes due to the mutual solubility of the two liquids have been allowed for in the calcualtions of these interfacial tensions.

[v] Of these boiling points the absolute values are uncertain.

[z] Here the interfacial tension is decreasing rapidly; these values are the extrapolated values at time zero, i.e. at the start.

alkali solutions,—if anything to a less extent in the solutions than in the pure water. But the density changes resulting from the solution of oils in water are less than those resulting from the solution of water in oils. From the values of Table V, therefore, it was possible to forecast the change in (d − d′) due to mutual solution of an oil and a solution from the known change in (d − d′) due to the solution of this oil and water. In all the I.T. tables those interfacial tensions marked with an asterisk (*) are calculated from the densities of the mutually saturated liquids, and those not so marked are calculated from the densities of the original liquids. In many cases where (d − d′) decreased owing to mutual solubility of the two liquids during an interfacial tension experiment, the value of h was found to increase proportionately so that the value of I remained constant (v. eqn. 1). The constancy of the interfacial tension between many pairs of liquids over a considerable time of contact was thus satisfactorily proved, e.g. Table I, expts. 14, 28d, 30c, 38.

In the interfacial tension experiments the organic liquid sometimes became opalescent either throughout, or at the interface, or at its surfaces next the glass where a film of water (etc.) was left between the oil and the glass as the liquids were run into position. In many cases this opalescence was undoubtedly due to the solubility of water in the oil. This opalescence appeared more or less quickly after the contact of the two liquids; it generally started from the outer interface and spread therefrom through the oil; it sometimes, but not always, disappeared after some hours in the thermostat,—presumably as

TABLE II

Interfacial Tensions (dynes/cm.) at 30° of Oils and Water or Concentrated Salt Solutions

No.	Liquid	With Water	Salt Solution		With NaCl solution (Series S)			
		Initial I. T.	Density 30°/4°	%NaCl	Initial I. T.	Over hrs.	Final I. T.	After hrs.
		(Y)			(S)			
1′	Petrol	46.10	1.18544	25.34	54.36	1½	55.8	20
11	Isobutyl alcohol	2.1	1.19439	26.42	7.30	48	—	—
12b	Amyl alcohol	4.95	1.18685	25.51	10.52	½	9.5	20
13	Phenyl ethyl alcohol	4.51	1.19613	26.63	9.98	1	9.64	26
14	Acetophenone	12.00	1.18544	25.34	17.84	20	—	—
17	Acetic anhydride	3.4	1.17578	24.18	8.0	0	0	3½
18	Quinoline	2.87	1.19439	26.42	9.93	47	—	—
19′	Aniline	6.00	1.18685	25.51	12.1	1	—	—
25a	Ethyl acetate	6.79	1.17955	24.635	14.50	22	14.50	22
32a	Benzyl acetate	15.41	1.17955	24.635	21.12	3	21.50	22
34	Isobutyl benzoate	(24.1)	1.19234	26.175	30.57	24	30.28	24
35a	Benzyl benzoate	25.41	1.19480	26.47	31.53	2	31.07	24
39	Ethyl acetoacetate	3.75	1.19480	26.47	10.90	2	10.2	48

TABLE III

Interfacial Tensions (dynes/cm.) at 30° of Oils and Water or Acid or Alkali Solutions

No.	Liquid	With Water	Series X With 1.03 N. Hydrochloric Acid				Series Y With 2.796 N. Sulphuric Acid				Series Z With 1.024 N. Sodium Hydroxide			
		Initial I. T. (γ)	Initial I. T. (x)	Over hrs.	Final I. T.	After hrs.	Initial I. T. (y)	Over hrs.	Final I. T.	After hrs	Initial I. T. (z)	Over hrs.	Final I. T.	After hrs.
1′	Petrol	46.10	45.90	19	45.7	19	46.80	19	46.8	19	47.22	½	43.70	19
											†39.6	–	†24.45	19
14	Acetophenone	12.00	—	—	—	—	12.46	2½	10.87	22	14.20	1½	14.64	25
16x	Benzaldehyde	14.1	—	—	—	—	12.57	1½	14.73	47	† 7.4	0	† 3.2	24
19′	Aniline	6.00	—	—	—	—	—	—	—	—	8.52	6	—	—
25b	Ethyl acetate	6.39	6.84	¼	0	18	—	—	—	—	7.02	¼	6.06	19
26b	Butyl acetate	8.10	7.60	4	6.1	24	—	—	—	—	9.20	1½	7.64	20
27a	Amyl acetate	10.88	—	—	—	—	—	—	—	—	12.4	¼	10.43	98
27b	Amyl acetate	12.05	12.10	¼	10.93	98	—	—	—	—	—	–	—	—
28a	Ethyl butyrate	12.45	12.36	1½	6.90	72	—	—	—	—	12.9	¼	11.36	24
28b	Ethyl butyrate	13.54	13.50	½	8.71	48	—	—	—	—	—	–	—	—
29b	Amyl butyrate	20.78	20.34	5	19.82	75	20.47	3	19.7	72	16.58	2	17.02	75
30b	Amyl valerianate	19.52	19.76	2	18.13	19	—	—	—	—	14.27	½	15.0	19
31a	"Oenanthic ether"	19.55	20.47	1½	19.3	72	—	—	—	—	—	–	—	—
32a	Benzyl acetate	15.42	—	—	—	—	15.76	7	15.80	72	—	–	—	—
33	Methyl benzoate	16.63	16.86	½	15.4	72	—	—	—	—	13.15	0	10.1	18
34	Isobutyl benzoate	24.1	—	—	—	—	24.61	¾	24.85	24	13.47	¼	12.85	1
35	Benzyl benzoate	25.68	—	—	—	—	—	—	—	—	11.2	½	—	—
37	Amyl salicylate	29.98	—	—	—	—	29.3	¼	25.7	45	—	–	—	—
38	Ethyl phthalate	14.64	14.71	2	14.45	72	—	—	—	—	8.4	¼	10.88	22
39	Ethyl acetoacetate	3.75	—	—	—	—	—	—	—	—	3.31	½	—	—
39′	Ethyl acetoacetate	3.50	—	—	—	—	4.14	1	1.65	65	—	–	—	—

† These experiments with 1.339 N sodium hydroxide solution.

TABLE IV

Some Varying Interfacial Tensions at 30°

No.	Organic liquid	Aqueous liquid	Interfacial tension (dy/cm after hours:— 0	$\frac{1}{4}$	1	3	18	limiting
16Z	Benzaldehyde	1.3N. NaOH	7.4	5.36	4.84	3.9	3.3	3.2 (24 hrs.)
17	Acetic anhydride	Water	3.1	0.96	—	—	—	0 (28 mins.)
17′	" "	"	3.7	1.27	—	—	—	0 (29 mins.)
(17)	" "	Water at 7.5°	3.15	2.8	1.5	—	—	0.6 (2 hrs.)
17′S	" "	24% NaCl	8.0	7.8	5.9	[3.2 (2 hrs.)]		0 ($3\frac{1}{2}$ hrs.)
25bX	Ethyl acetate	N. HCl	6.84	6.84	6.22	4.9	0	2.8 (10 hrs.)
25bz	" "	N. NaOH	7.68	7.02	6.55	6.38	6.06*	———
28bx	Ethyl butyrate	N. HCl	—	13.5	13.0	12.3	10.3	8.7 (48 hrs.)
33z	Methyl benzoate	N. NaOH	13.15	12.76	12.4	11.8	10.1	———
37Y	Amyl salicylate	2.8N. H_2SO_4	—	29.3	28.5	28.0	26.7	25.7 (45 hrs.)
39′	Ethyl acetoacetate	Water	3.50	3.45	3.35	3.25	—	3.18 (26 hrs.)
39′Y	" "	2.8N. H_2SO_4	—	4.14	4.14	3.6 *	2.7	2.5 (38 hrs.)
								1.65 (65 hrs.)
39	" "	Water	3.75	3.58	3.41	3.16	2.9	2.9 (49 hrs.)
40	Maize Oil	Water	—	5.8	3.0	1.7	0	0 (8 hrs.)
40a	" "	"	—	8.95	5.33	2.2	0	0 (18 hrs.)
40′	" "	"	—	20.7	20.0	19.6	19.2	———
41	Cotton Seed Oil	Water	—	22.4	22.0	21.7	20.8	20.8 (24 hrs.)
42	Sperm Oil	Water	—	5.70	5.05	4.31	3.67	3.57 (24 hrs.)
42a	" "	"	—	3.91	3.36	3.02	2.73	———

the oil became saturated with water. But why should there be any opalescence under the circumstances, i.e. at constant temperatures? Does emulsification precede true solution? Further it was the general rule for the oils, clear and saturated with water, to become opalescent after cooling—either after the I.T. or density determinations. This is readily explained by the decreasing solubility of the water in the oil as the temperature fell. The only liquids (of Table V) that after saturation with water did not become opalescent after cooling, were the petrols and the phenyl-ethyl-alcohol.

However, in the I.T. experiments with water opalescence only occurred with 17 out of the 42 liquids, and similarly with the acid solutions: it occurred in none of the experiments with the concentrated salt solutions, and in half of the experiments with the caustic soda solutions, and in none of the cases where there is great mutual solubility,—e.g. experiments 11-14 and 17 and 25-28. This opalescence, due to solution, occurs in the primary stage therof, and where solution is great this stage presumably is soon passed. There were no obvious relations between this opalescence and the purity of the oil, the density changes due to mutual solution, and the variations observed in the I.T.

But opalescence may sometimes be due to special impurities thrown out of solution from the oil by solution therein of water, e.g. expts. 7, 10, 16; v. notes, later.

And opalescence is undoubtedly due in certain cases with the solution of sodium hydroxide to chemical action with the oil, i.e. its saponification and separation of the soap, mainly at the interface, e.g. with the liquids 31, 33, 34, 37. This is the case too with the fatty oils and water, e.g. 40a and the 1922 oils (loc. cit.). Such opalescence attains its maximum intensity at the interface, giving there finally a crinkled, quite contaminated and often semi-solid interface. Here there is decreasing and variable interfacial tension. This last opalescence, that due to the dissemination of insoluble products of interaction between the oil and the solution, was noted in our previous paper; but the former opalescence, due to the first solution or dissemination of the water in the oil, was not noted.

In Table I are given the densities and boiling points of the organic liquids used. In most cases they were distilled and the boiling points were determined by carefully standardised thermometers and are correct to within fractions of a degree Centigrade. The initial interfacial tension was generally calculated from the mean value of h obtaining over one or two hours and during the first four or five settings. But in certain cases where the variations in h were small and not definitely in one direction, the mean value of h over the whole period of the experiment was used to calculate the initial interfacial tension; here a final interfacial tension may or may not be given. The final interfacial tension was usually calculated from the densities of the saturated liquids and marked with an x in the table; where they have been calculated from the densities of the original (unsaturated) liquids, the final interfacial tensions will be less accurate.

Variations in the interfacial tension between two liquids must be due to changes; (a) in the liquids due to mutual solubility; (b) in (or at) the interface due to the concentration there of suspended or dissolved substances from the contiguous liquids, or (c) in the two liquids due to chemical action between them, e.g. the development of acidity in aqueous layers from the hydrolysis of esters. Now the effect of (a) must be instantaneous, i.e. at the interface between two liquids mutual saturation must be rapidly completed. This is obvious from the present experiments, and it is well confirmed by Reynolds' measurement of the surface tensions of saturated liquids by placing one of them in a reservoir and capillary tube in a closed space saturated with the vapour of the second, loc. cit., p. 467. Thus on making contact between two liquids it is impossible to distinguish between (1) the I.T. between the original liquids, (2) the I.T. between the saturated interfaces or accommodated interfaces, and (3) the I.T. between the saturated liquids with saturated interfaces. In the present capillary tube method (3) is only marked from (2) by the related changes of h and (d − d′), on allowing for which (3) = (2). But it is in general possible to note the further stage, when the saturated liquids have evolved a contaminated interface carrying adsorption products or products of reaction due to (b) or (c). These effects are cumulative and generally slow enough to observe.

The conclusions from the interfacial tension experiments are as follows, certain particular cases being referred to in detail under the special notes about each organic liquid (p. 805 et seq.). From the results of Table I of the I.Ts. with water it will be seen that:—

(a) The oils of variable I.T., 7 samples, are impure oils, e.g. 16, or oils suffering chemical changes, e.g. 5; here the average variation observed in the I.T. over the time of contact was 10% of the value.

(b) The oils of decreasing I.T. are the fatty oils, 40 to 42, the oils of greatest solubility in water, 11, 12, 17, 19 and 39, certain oils that are complex mixtures, e.g. 5′, 7, 9, 29, and oils that react chemically with the water, e.g. 5′, 24, 26, 39. Here the average variation in I.T. is from 1 to 100%; there are 32 cases of this type.

(c) The oils of increasing I.T. are rare,—14 samples. Special reasons operate for the terpenes, 6 & 6a, and for the three petrols, 1a, 1b, 1c. Many of the remaining nine cases approximate to constant I.T.,—the average increase of I.T. being 2% of the I.T. value.

(d) The oils of constant I.T., 25 samples, are the purest liquids, usually with not too great solubility in water, e.g. 2, 3b, 14, 21, and 32b, and certain oils that are mixtures, e.g. 28, 29b, 30c and 31. Here the average variation of I.T. is 1.6% (from 0.2 to 6%),—partly depending on the absolute value of h.

It may be concluded that:—

(1) Purification of an oil tends to produce a more constant I.T.; e.g. 1b to 1d, 5 to 5a, 30 to 30c, 35 to 35a. With two pure liquids, where there is no chemical action or excessive mutual solubility, the I.T. is constant over a long period; in the present experiments the variation in the I.T. in such cases over one to three days does not exceed 1% of the initial I.T.

(2) A mixed oil has often a similarly constant I.T. against water or a solution; e.g. expts. 1′, 28 a, b, c and d, 29 to 31b, and also 32a, 32aY and 32aS, 34Y etc.

(3) Evidently a mixed oil only gives a varying I.T. against water or a solution where selective adsorption, or concentration, at the interface occurs with some of the components of either or both of the liquids in contact, or where chemical action occurs that results in such adsorbable products. Experiments 1′ and 1′Y (with constant I.T.) contrast with experiments 1′Z, 1a, b, c, and d (with varying I.T.). Such selective adsorption is partly the reason why the fatty oils and water give decreasing I.Ts.; thus the filtered maize oil, 40a, gives a higher and slower varying I.T. with water than the original oil, 40. For I.Ts. against colloidal solutions see Reynolds, loc. cit.

(4) Apart from the variability of the I.T., however, purification of an oil tends to raise the I.T.; e.g. 1b to 1d, 3a to 3b, 25 to 25a and 25b.

(5) In most cases, however, the I.T. of oil-solution tends to rise with the higher fractions of the oil quite apart from purification; e.g. with oils 26 to 31.

(6) A mixture of oils often has a lower I.T. against a given solution than the average I.T. of the components. Thus with the amyl butyrate the mean value of the I.Ts. of the fractions is 19.3 and the original liquid has I.T. of 17.7; this is a rough test as initial and final fractions were rejected; the ethyl acetate and amyl valerianate, however, similarly confirm the rule.

(7) The greater the mutual solubility between two liquids the lower is the I.T. Thus oils have lower I.Ts. against salt solutions than against pure water; and the following groups of liquids are in order of decreasing solubility and increasing I.T.,—benzene, toluene and xylene; isobutyl, amyl and phenylethyl alcohols; ethyl, butyl, amyl and benzyl acetates (v. Seidell's "Solubilities"). The I.T. = S.T.$_{A'}$ − S.T.$_{B'}$, where S.T.$_{A'}$ is the surface tension of the liquid, A, saturated with the liquid, B, and S.T.$_{B'}$ is that of B saturated with A,—Reynolds' rule (loc. cit.); when the liquids are completely miscible S.T.$_{A'}$ = S.T.$_{B'}$ and the I.T. = O. The difference between the S.Ts. of the pure liquids, S.T.$_{A}$ − S.T.$_{B}$, gives the maximum possible I.T. between them, that which would obtain if they were completely immiscible. The more the observed I.T. is less than (S.T.$_{A}$ = S.T.$_{B}$), the greater is the mutual solubility. Where the mutual solubility is great this method of measuring the I.T. is unsuitable, unless the liquids were mutually saturated beforehand.

Table II gives the interfacial tensions at 30° of thirteen liquids against concentrated solutions of common salt in water. From the density of the salt solution the percentage weight of salt therein was taken from the Landolt-Börnstein tables. The conclusions are as follows.

(8) The I.T. of an oil against the salt solution is greater than its I.T. against water at the same temperature, or $I < s$. These salt solutions are approximately of the same concentration, and $s = 1.07 \, . \, I + 5$—(2). A relation like this equation (2) can be deduced from Reynolds' rule. Let S.T.$_{S}$, S.T.$_{O}$, and S.T.$_{W}$ be the surface tensions of the salt solution, oil and water

respectively; then, after Reynolds, if the mutual solubility is negligible,— $s = S.T._S - S.T._O$, and $I = S.T._W - S.T._O$, and thus $s - I = S.T._S - S.T._W$ = a constant. Now at 30° $S.T._W = 71.5$ and the S.T. of a 25% salt solution = 80.5 (dynes per cm.), so that $(s - I) - 80.5 - 71.5 = 9$. Equation (2) approaches this with liquids of high I.T.

(9) With a given oil the variation of the I.T. against a salt solution is usually less than the variation of its I.T. against water. The experimental error is probably greater with the salt solution than with water, but the lower solubility of the oil in the salt solution is the cause of this I.T. behaviour. The oil also would take up less water from the salt solution than from pure water; also hydrolysis of an oil would be less rapid with a salt solution than with water. From equation (2) and the values of s for the isobutyl alcohol and isobutyl benzoate there have been obtained the values of I for these liquids, which values are in brackets in Table II.

Table III gives the interfacial tensions at 30° of organic liquids against the solutions of hydrochloric and sulphuric acids and the solution of sodium hydroxide. The following conclusions may be drawn.

(10) There are five cases of decreased initial I.T. with the hydrochloric acid solution, and six cases of increased I.T., the average increase being 0.33 dyne per cm., compared with the I.Ts. against water. The general behaviour is that the aqueous solutions of salts, acids and bases the I.T. of an oil is greater than with water, and the above cases of increased I.T. with the HCl solution are similar to the normal results recorded by other observers[1]. But all the oils examined by the author gave with the HCl solution I.Ts. decreasing with time, and thus the initial I.Ts. given in Table III may be rather low.

(11) With the normal hydrochloric acid solution the interfacial tension of an ester varies more than the I.T. with water, the former I.T. decreasing with the time and from two to fifty times more than the corresponding decrease (if any) of the oil-water I.T. Now the experimental errors are not greater—at any rate, not 5 or 50 times greater—with the solutions than with water, and should not lead always to decreasing I.Ts. in the former cases. Also the mutual solution is rather less with the esters and the acid solutions than with the esters and water (Table V). The varying decreasing I.Ts. of the esters and the acid solutions must then be due to the adsorption at the interfaces of the products of the hydrolysis of the esters. The alcohols, resulting from the hydrolysis, will increase the mutual solubilities of the two layers[2] and therefore decrease the I.Ts.; this effect will be the more pronounced with the alcohols of lower molecular weight. The presence of the lower fatty acids, too, will produce probably the same effect. Esters of the lowest molecular weight have the greatest velocities of saponification[3] and it is these esters that with HCl solution give the most rapid decrease of I.T.,—though the mutual solubilities are the greatest with these also. In contact with water for

---

[1] See Harkins and others: J. Am. Chem. Soc., (1916-1917); Reynolds: loc. cit.

[2] Seidell: "Solubilities".

[3] Reicher: J. Chem. Soc., **48**, 1034 (1885).

TABLE V

Densities (30°/4°) of mutually Saturated Liquids

Liquids	Number	Densities Satd. Oily Layer	Satd. Aqueous Layer
From special tests:—			
Petrol—Water	1a	0.6692	0.9955
Petrol—Water	1b	0.71025	0.99564
Petrol—Water	1c	0.73146	0.99566
Benzene—Water	2	0.86708	0.99563
Toluene—Water	3b	0.85164	0.99561
Amyl alcohol—Water (0.80398)	(12)	0.82167	0.99167
Aniline—Water (1.01302)	(19)	1.01385	0.99716
†Chloroform—Water (1.4897)	(20)	1.4831	1.0002
Carbon tetrachloride—Water (1.57432)	(21)	1.57412	0.99594
Nitrobenzene—Water (1.19189)	(22)	1.19120	0.99600
Chlorobenzene—Water	23b	1.09533	0.99577
From I.T. Tests:—			
Petrol—Water	1d	0.7100	0.9957
Petrol—Water	1′	0.72774	0.99569
Turpentine—Water	5′	0.85215	0.99581
Pine Oil—Water	8	0.92308	0.99567
Phenyl-ethyl alcohol—Water	13	1.01082	0.99577
Acetophenone—Water	14	1.01979	0.99571
” —H_2SO_4	14Y	1.01977	1.07972
” —NaOH	14Z	1.01993	1.03907
Benzaldehyde—H_2SO_4 (1.04855)	16Y	1.04710	1.08104
” —NaOH (1.03838)	16Z′	1.03548	1.05415
Ethyl acetate—Water	25b	0.89397	0.99484
Butyl acetate—Water	26b	0.86609	0.99316
” —HCl	26bX	0.86678	1.01254
Amyl acetate—Water	27b	0.85963	0.99556
” —HCl	27bX	0.85968	1.01348
” —NaOH	27aZ	0.85589	1.03824
Ethyl butyrate—Water	28a	0.87753	0.99535
” —Water	28b	0.87587	0.99550
” —HCl	28bX	0.87721	1.01309
Ethyl butyrate—NaOH	28aZ	0.87719	1.03815
Amyl butyrate—Water	29b	0.85833	0.99559
” —HCl	29bX	0.85835	1.01345
” —NaOH	29bZ	0.85799	1.03847
Amyl valerianate—Water	30c	0.86171	0.99579
” —HCl	30bX	0.86053	1.01345
” —NaOH	30bZ	0.85948	1.03836

† For chloroform and water the figures are specific gravities at 22° by Herz,—from Seidell's "Solubilities".

TABLE V (continued)

Liquids	Number	Densities Satd. Oily Layer	Satd. Aqueous Layer
"Oenanthic ether"—HCl	31aX	0.85968	1.01356
Benzyl acetate—H_2SO_4	32aY	1.04611	1.08033
Methyl benzoate—Water	33	1.07786	0.99570
Isobutyl benzoate—H_2SO_4	34Y	0.98958	1.07959
" —NaOH	34Z	0.98954	1.03832
Benzyl benzoate—Water	35a	1.10745	0.99565
Amyl salicylate—Water	37	1.04207	0.99561
" —H_2SO_4	37Y	1.04226	1.07959
Ethyl phthalate—Water	38	1.10929	0.99569
" —HCl	38X	1.10935	1.01349
" —NaOH	38Z	1.10906	1.03830
Ethyl acetoacetate—Water	39′	1.01840	0.99643
" —H_2SO_4	39′Y	1.01160	1.0803 (?)

Densities of the Aqueous Solutions at 30°:—

Solution	Density$\left(\frac{30°}{4°}\right)$	Normality at 15°	% Solute approx.	Series
Water	0.99567	0	0	—
Hydrochloric acid	1.01351	1.030	3.69	X
Sulphuric acid	1.07957	2.796	10.2	Y
Sodium hydroxide	1.03831	1.024	3.6	Z
Sodium hydroxide	1.05200	1.339	4.9	Z′

several days these esters gave increasingly acid solutions, but the effect of this hydrolysis on the I.T. of the ester-water is slight and not to be distinguished, in general, from those of other disturbing causes such as solubilities and impurities. But with the HCl solution, which accelerates the saponification (as is well known), the effect of the latter is enhanced.

(12) The interfacial tension, y, of an oil against the 2.796 Normal sulphuric acid solution is greater than its I.T., I, against water, and excepting the benzaldehyde and the amyl salicylate, $y = 1.017 . I$,—(3).

(13) With oils insoluble in and unacted on by both water and the sulphuric acid solution, the variations in the interfacial tensions will be the same in the both cases, e.g. with petrol. With the H_2SO_4 solution and acetophenone, benzaldehyde and ethyl acetoacetate the variation in the I.T. was large; in the last case chemical action was undoubted and in the former two cases most probable. With the esters and the H_2SO_4 solution there is, in general, a decrease in the I.T. with time, which is comparable to that occurring with the HCl solution.

(14) There is no simple relation between the I.T. of oil-water and that of the oil against the sodium hydroxide solutions. Taking the initial I.T. of petrol with the 1.024N NaOH solution as showing the normal rise of I.T.

with this solution compared with water, then the lower esters show a greater rise proportionately, and the higher esters—the last seven liquids in Table III, series Z—show not even a rise but a considerable lowering of I.T. from the oil-water I.T.

(15) With the sodium hydroxide solutions the variations in the interfacial tensions of the oil are large; here the I.Ts. usually decrease with time. In many cases the capillary meniscus lags behind on making a fresh setting and h is temporarily large; the meniscus behaves as if it were filmed, and contamination of the meniscus is evident with the last five esters of the series Z. Here, then, the variation of I.T. is larger with the higher than with the lower esters; also for the lower esters the I.T. variation with the normal alkali solution is less than that with the normal acid solution but greater than that with water. But for the higher esters the I.T. variation with the alkali solution is greater than that with the acid solution and much greater than that with water.

The case of petrol with the normal alkali solution may be taken to indicate that the merest traces of saponificable impurities in an oil greatly lower the I.T. from that with water after contact for some time; and possibly traces of soaps or similar substances (e.g. sodium silicate) in the alkali solution will be adsorbed at the interface and do likewise,—see the result with petrol and the 1.339 N solution of alkali. The higher esters give low I.Ts. with the alkali solutions, for any acids of high molecular weight, traces of which are present in them originally or are formed by their hydrolysis, will form soaps with the alkali and thus lower the I.T. Similarly with the benzaldehyde that contained some benzoic acid. The esters of lower molecular weight, e.g. the acetates, form (sodium) salts of little soap-like character; here the initial I.T. is higher than with water—the normal behaviour, and the decrease of the I.T. with time is less than with the higher esters. Under equal conditions, the higher esters are the less rapidly hydrolysed, but the products formed from them have the greater power of decreasing the I.T. and in extreme cases the contamination of the menisci is quite evident. Certainly the hydrolysis of esters by acid and alkali solutions, and to a much smaller extent by water, is one factor which causes their decreasing I.Ts. The large decrease of I.T. with the lower esters and the normal HCl solution is due to this cause supported by the added one of increased mutual solubility due to the products of the hydrolysis; and the large decrease of I.T. with the higher esters and alkali solutions is due to the hydrolysis and to the soaps formed thereby.

Notes on the Organic Liquids used, Their Purity, Interfacial Tensions, etc.

In this section the facts will be condensed as much as possible, and standard abbreviations used often, e.g. b.p. for boiling point, S.T. and I.T. for surface and interfacial tension. After the organic liquids had been shaken with water at the ordinary temperature or merely kept in contact therewith at this temperature or at 30° (including the I.T. tests themselves), the acidity or alkalinity of the water was frequently tested by litmus paper (and sometimes by methyl orange); these tests will be generally referred to later to indicate the purity or hydrolysis of the organic liquid. The numbering of the oils (organic liquids) and samples corresponds with that of the tables.

(1) "Plume Benzoline", from the Vacuum Oil Co., was divided into the distillate boiling between 40° and 70° and the residue; these fractions were of approximately equal bulk. They were then fractionated separately; the b.p. rose regularly throughout each fractionation. From the former, after discarding the more volatile fraction, was collected *petrol 1a*, in bulk about 3/10 ths of the original benzoline. From the latter, after discarding the first distillate, were collected *petrol 1b* and *petrol 1c*. These petrols, from Pennsylvanian petroleum, presumably consist of the paraffins,—hexane, heptane, etc. With these petrols and water h increased with time; the density changes did not account for the rise in h, and thus the I.T. increased. However it was found later that each of these petrols gave with water an acid solution. The cause of this acidity was not obvious. Then fresh samples of petrol were prepared. The samples 1a, 1b, and 1c, after use as above, were dried with $CaCl_2$ and bulked; this liquid was filtered on to K_2CO_3, and after 16 hours was filtered off and distilled. The first third was rejected and then one-half was collected as *petrol 1d*. Another sample of commercial petrol, which gave with water a solution practically neutral or very feebly acid, was distilled; one-fifth of it was rejected and then one-half was collected as *petrol 1'*. Petrols, 1d and 1', gave with water neutral solutions, even after four days' contact with water in the I.T. apparatus. With water and the petrols, 1d and 1', h was constant over 5 settings in the first two hours, but after 16 hours h had decreased. With sample 1d this decrease continued to the third day, after which h remained constant for another 24 hours. With sample 1' h increased after 16 hours but very slowly after the third day. The final I.T. was a little greater than the initial I.T., but this might be within the limits of the experimental errors, so that this petrol might be considered to have a constant interfacial tension with water. With the NaCl, aq. the rise of I.T. was more pronounced; after the test the solution was neutral. With this petrol and the NaOH, aq. h was variable; it was constant in the first set over half an hour; in each succeeding setting the initial value of h increased, but during each setting h decreased. With the 1.339 N. NaOH, aq. the variations in h were still greater.

In a paper on I.T. between petroleum products and water, E. M. Johansen[1] states that the presence of small amounts of organic acids in the former affects their I.T. against water and dilute alkali solutions. Shoeter and Ellingsworth[2], state that Donnan showed that with a hydrocarbon oil to which a little fatty acid had been added, the I.T. of the oil-alkali solution was much lower than that of the oil-water, but with an ordinary hydrocarbon oil, i.e. free from fatty acid, the oil-water I.T. is little affected by addition of alkali. Judging from Harkins and Humphrey's work, the I.T. between a hydrocarbon oil and water is raised by addition of mineral acids and salts to the water, lowered by organic acids (the lowering increasing from formic to butyric acid), lowered by the first additions of alkali and then raised by further additions (above 1/100 or 1/10th normal) of alkali; also the I.T. is greatly lowered by small additions of soluble soaps (e.g. sodium oleate below 1/100 normal).

---

[1] J. Ind. Eng. Chem., **16**, 132 (1924).

[2] Proc. Roy Soc., **92**, 231 (1916).

It might be concluded that petrol 1′ even after careful distillation contained traces of impurities, possibly volatile fatty acids, that caused the variable and, in general, diminishing I.T. against alkali solutions, and that with the 1.3 N NaOH, aq. there might be further impurities in this solution which were not present in the normal solution. Even the petrol 1d, which was twice distilled besides being treated with K_2CO_3, gave with water an I.T. much more variable than would be expected. The interfacial tensions of hydrocarbon oils against water or aqueous solutions seem to be extraordinarily sensitive to minute amounts of impurities.

(2) The *benzene* was that carefully purified in 1922. On shaking with water or after keeping with water for two years, it gave a solution neutral to litmus. Its density (Table I) was unchanged after keeping. The I.T. of this benzene-water could be considered constant over 20 hours; the value in Table I is somewhat higher than the I.T. found in 1922, and there was some tendency for this I.T. to decrease with time.

(3) Commercial toluene was treated with P_2O_5 for twelve hours and then fractionated. The first reaction made *toluene* 3*a*; the second fraction, *toluene* 3*b*, was the main one and in bulk was about one-half of the original liquid. These toluenes had similar b.ps. to the 1922 samples, but lower densities and lower I.Ts. with water, indicating that the present samples were the less pure. Toluene 3b after 17 hours' contact with water at 30° gave a slightly acid solution; sample 3a was probably similar.

(4) Xylene was shaken for a few minutes with P_2O_5 and then fractionated. The first fraction was neglected; *xylene* 4*a*, the next fraction, was the main lot; *xylene* 4*b*, the next fraction involved boiling nearly to dryness. The three isomers were doubtless present in both samples, 4b being the more homogeneous (m-xylene). Both samples gave neutral solutions with water, but the I.T. behaviour indicated that 4b was the purer or the more homogeneous.

(5) *Turpentine,* 5, was the distilled American turpentine of 1922 (b.p. = 160.6°). It had been kept for two years in a corked bottle but not secure from oxidation, which certainly had occurred. The liquid now had a deeper yellow colour, and the glass in contact with it had been attacked and permanently roughened. The density at 30° had increased from 0.85460 to 0.91207. The variations in h were fairly large; evidence was seen of solution and of density changes, and the apparent constancy of the I.T. was certainly the result of the balancing of several factors, e.g. the lowering of the I.T. due to contamination of (or adsorption at) the interface, the raising of the I.T. due to the water becoming acid, changes in (d—d′) etc. A minimum I.T. of 8.5 dy/cm was obtained after a long setting of 17 hours, and then the menisci were flat. These I.Ts. are less than one-half of the 1922 values. Reynolds also found that the

I.T. of turpentine-water decreased with the age of the turpentine, when the latter was kept exposed to air.

This turpentine was placed for an hour or so over $CaCl_2$, filtered and distilled. It frothed over at the start, probably due to decomposition, and then about two-fifths of the original liquid was collected as a slightly milky distillate, which however became clear on passing through filter paper,—preferential adsorption of water (?). The distillate was *turpentine* 5*a*; it gave a strongly acid solution with water. It like all the terpenes (oils 5 to 10) showed variable I.T. with water, but the I.T. was greater and its variability was less with this distilled and purer turpentine 5a than with the original turpentine 5.

Turpentine, 5′, was a colorless American turpentine, which was filtered only before testing. It had $D^{14°}_{4°} = 0.865$ and $[\alpha]^{14°}_{D} = +19.9°$. It gave with water a neutral or very feebly acid solution, but the aqueous solution from the I.T. test after 18 hours was feebly acid and after 46 hours quite acid. The minimum I.T. observed was 9.5 dy/cm, after 18 hours.

Terebene, 6, from Howards and Sons, London, was used straight from the bottle. It was very pale straw-colored, gave a strongly acid solution with water, and had $D^{14°}_{4°} = 0.871$ and $[\alpha]^{14°}_{D} = -6.0°$. The I.T. decreased slightly in each setting.

This was shaken with $CaCl_2$ for half an hour, filtered and fractionated. About one quarter came over as a milky liquid from 168.5° to 174°, then one-half collected as *terebene 6a*. This was made quite clear by filtering and standing; evidently some decomposition accompanies the distillation. It gave a strongly acid solution with water, and had $D^{14°}_{4°} = 0.866$ and $[\alpha]^{14°}_{D} = -5.2°$. Its I.T. behaviour was similar to that of the original terebene 6; compare experiments 6 and 6a with experiments 5 and 5a.

Limonene, 7, was prepared from Sicilian oil of lemon by distillation under reduced pressure. This sample probably contains about ten per cent of terpenes other than limonene. It was light straw brown in colour, and had $[\alpha]^{15°}_{D} = +65°$. It gave with water an acid solution.

Pine oil, 8, was "standard A" oil from Georgia, U. S. A. It was a clear yellow, somewhat viscous oil, and gave with water an acid solution—the acidity being more pronounced after prolonged contact. It had $D^{13°}_{4°} = 0.937$ and $[\alpha]^{13}_{D} = +2.00°$. h increased with time rather more than (d—d′) decreased, so that the I.T. increased.

Eucalyptus oil, 9, was from Maryborough, Victoria. It was a colorless oil, containing 75% cineol, and had $D^{13°}_{4°} = 0.920$ and $[\alpha]^{13}_{D} = +1.28°$. The water from the I.T. test was feebly acid. This oil was similar to the (cineol) eucalyptus oil of 1922.

Cineol, 10, was separated from the above oil by phosphoric acid; the cineol-phosphate was pressed dry, washed with petrol, decomposed with water; the separated cineol was washed with water, dried over $CaCl_2$ and filtered before use. It was a yellowish oil; exposed to a temperature of −8° for one hour it did not freeze at all; thus it was not pure cineol, of which the accepted melting point is −1°. In the I.T. test h was very variable; in each setting h decreased for the first few minutes, then increased for about 20 minutes, and then in the last setting decreased over 18 hours. After a few minutes contact with water, the cineol became opalescent at the interface, and this finally spread throughout the whole of the cineol and little drops appeared at the outer meniscus. It might be supposed that as the cineol became saturated with water, it deposited some other component (petrol, phellandrene, etc.). In Table I the initial Y is the initial and minimum value in the first setting, which was also the mean of the minimum values in the first three settings over one hour; maximum recorded Y = 10.1, and the final value after 20 hours = 6.6 dy/cm. For giving the I.T. of pure cineol these figures are worthless but they illustrate the possible variations in I.T. of a complex mixture. Isobutyl alcohol,—from E. Merck, Germany, was placed with anhydrous K_2CO_3 for several days, then filtered and fractionated. The liquid boiled from 104° and about two-thirds was distilled off till the rate of increase in the b.p. slackened and then was collected the *isobutyl alcohol*, 11, in bulk about one-fifth of the original. This sample has constants agreeing with Perkin's isobutyl alcohol[1]. It gave a neutral solution with water and was optically inactive. It was too soluble in water for any I.T. therewith to be obtained directly with accuracy, the value (1.5 dy/cm) quoted in Table I being merely indicated,—h being very small and soon zero and the menisci flat and vanishing. Against concentrated salt solution it gave a constant I.T., from which the I.T. with water may be taken as 2.1 dy/cm.

(12) *Amyl alcohol*, from Merck, was treated with K_2CO_3 for 12 hours, then filtered and fractionated. After rejecting one-fifth, the rest was collected in two equal lots as samples 12a and 12b. These samples of amyl alcohol were slightly laevorotatory, $[\alpha]_D^{14} = -0.9°$; they were mainly inactive isobutyl carbinol with a little of the active variety and of other isomers. They gave with water solutions acid to litmus. Amyl alcohol and water are appreciably mutually soluble, and the density changes due to such are considerable (Table V). In the I.T. tests with water for the first hour h and (d—d′) both decreased, but afterwards h was nearly constant. The 1922 samples of amyl alcohol were from a different source to the above; the results for them were recalculated and put in Table I as for samples 12′a and 12′b ,and they were similar to the above. At 16° the S.T. of water is 73.45, and the S.T. of the original Merck's amyl alcohol was 23.35, and thus the maximum I.T. (of the liquids before mutual solubility) would be 73.45 − 24.35 = 49.1 dy/cm; the much smaller I.Ts. observed reflect the great mutual solubility.

(13) *Phenyl-ethyl alcohol*, from L. Givaudan, Geneva, was purified by distillation, collecting about three-quarters of the original liquid as sample 13. This is presumably the normal alcohol, $C_6H_5 . CH_2 . CH_2 . OH$, though the b.p. was higher than the accepted figure,—212° in Atack's Year Book, 1918. Sample 13 was a clear, colorless, slightly viscous liquid with a faint smell; it was practically optically inactive; it was somewhat soluble in water (Table V) and the solution was neutral to litmus even after 25 hours contact with the alcohol. The I.T. is practically constant with water or salt solution.

---

[1] J. Chem. Soc., 45, 421 (1884).

(14) Commercial *acetophenone*, from Givaudan, was a slightly straw-colored liquid. It was distilled, the first quarter rejected, and then sample 14 was collected—in bulk about one-half of the original liquid. This gave with water a solution neutral or very feebly acid, even after 24 hours contact in the I.T. apparatus. In the I.T. tests with the salt, acid and alkali solutions the variations in h were more irregular than might have been expected. With the H_2SO_4, aq. I.T. test some turbidity was noticeable and the menisci tended to flatten, and the I.T. decreased. Is there any chemical action here? With the alkali solution h and (d—d′) both increased with time, so the I.T. increased; here no turbidity was observed.

(15) A small amount of Merck's "purest furfurol", kept in sealed vessels filled with hydrogen, was distilled. All of the distillate was taken, and a trace of moisture in it was removed by filtering. This sample of *furfural*, 15, was of pale straw-yellow colour and gave with water a neutral solution. The I.T. was practically constant; h, which was always small, showed a tendency to increase with time, probably due to density changes as furfural is somewhat soluble in water.

(16) *Benzaldehyde*, from Schuchardt, was purified by distillation in air, and consequently the product certainly contained some benzoic acid due to oxidation. Samples 16 and 16′ were from different stocks; with water both gave solutions acid to litmus but probably sample 16 was the purer. However the I.Ts.of the two samples were more constant and closer than might have been expected, considering the benzoic acid as a variable impurity and the density changes which were considerable (Table V). The supply of this material was limited; otherwise it would be an interesting one to study.

The sample 16′ after keeping a couple of months in a stoppered bottle was found to contain some crystals of benzoic acid. The latter were filtered off, and the filtrate had $D^{30^\circ}_{4^\circ} = 1.04855$,—a considerable increase over the density of the original sample. This filtrate, which must have been saturated with benzoic acid, was used in an I.T. experiment with the H_2SO_4 aq.. Here was turbidity, sticking of the capillary meniscus, and chemical action?

Other benzaldehyde that had been kept under water for two months, was separated therefrom and used in an I.T. experiment with the 1.339 N. NaOH, aq.. This water-saturated benzaldehyde had $D^{30^\circ}_{4^\circ} = 1.03838$, and presumably contained less dissolved benzoic acid than the preceding lot. Here the I.T. (z) decreased continuously; the outer meniscus was at first flat and than concave downwards (the reverse of the usual, when the organic liquid is introduced from the top of the apparatus). No turbidity was noticed, but the final alkali solution was yellow; in this case there was probably chemical action,—at least with the alkali and the benzoic acid impurity.

(17) *Acetic anhydride* was shaken for some minutes with P_2O_5, then filtered and fractionated. The original of sample 17 was from Merck, and that of sample 17′ from May and Baker, London. With acetic anhydride and water h and the I.T. were always small and fell rapidly to zero. At 8° the S.T. of sample 17 was 33.85, and of sample 17′ was 34.05; the S.T. of

water at 8° is 74.65, so that the maximum possible I.T. with water at 8° should be 40.8 dy/cm.. The observed low I.T. points to great mutual solubility. But the hydrolysis of acetic anhydride results in the formation of acetic acid, which is completely miscible with both the anhydride and water, and therefore certainly increases the mutual solubility of the latter liquids. The anhydride on shaking with an equal volume of water at 12° was completely miscible in an hour, but with equal volumes of water and acetic acid together it was immediately completely miscible. Thus the originally low I.T. decreases continuously on account of the increased mutual solubility due to the acetic acid produced by the hydrolysis. In a concentrated salt solution both the mutual solubility of the original liquids will be less and the rate of hydrolysis will also be less. In the I.T. experiments the lowering of h with time was faster with water at 30° than with water at 7.5°, and the lowering with concentrated salt solution at 30° was less than that with water at 7.5° (see Table IV). The I.Ts. given in the tables are the extrapolated values at time zero, i.e. at the time of first reaching the position or setting in the I.T. apparatus, but the liquids were of course in contact for some minutes before that. Slight irregularities occur for the first readings,—temperature and solution changes then; the final values of *h* also fall abnormally rapidly but many possible complications occur then. As no allowance was made for density changes due to the mutual solubility, the values of the I.Ts. must be only approximate.

(18) *Quinoline,* from the British Drug Houses Ltd., London, was distilled. It boiled at a constant temperature,—say 237.5° (Young), our thermometer being incorrect. About half of the original liquid was collected as *quinoline,* 18, a pale straw-colored liquid, which gave with water a neutral solution even after 5 months contact. When the organic liquid is heavier than water, it is introduced into the I.T. apparatus from the bottom upwards, and then the outer menuscus is higher than the capillary meniscus and both are convex upwards; this is the usual behaviour. Quinoline and water formed the only observed exeeption to that behaviour; in this case the menisci were concave upwards and nearly flat, and the capillary meniscus was the higher; when re-setting in the apparatus the outer meniscus might be raised momentarily above the capillary meniscus, but after the setting the latter soon rose up through the former and took up a position as before. Quinoline must have a great power of replacing water from glass surfaces; a study of such and of the contact angles would be interesting. Duplicate I.T. experiments were done with quinoline and water; in both h was small and its variations rather erratic; the general tendency was for h to rise with time,—a lag that obviously was related to the facts above. Quinoline and water, too, are somewhat mutually soluble, and the density changes (not determined) would also tend to make h rise. The initial I.T. given in Table I was the mean result of the two experiments. Over a longer period of time the results are less regular; in both experiments after 24 hours the Y approximated to 3.0 dy/cm. With salt solution the I.T. was constant over two days; here the quinoline was introduced from the top downwards and no irregularities (as with water) were observed.

The liquids, 19 to 22, were those prepared in 1922. The results in Table I for these liquids and water are taken from the writer's previous paper, the final I.Ts. being corrected for density changes and the boiling-points for thermometer errors. The *aniline* 19′, used with the salt and the soda solutions, was purified by distillation; it had $D_{4°}^{30°}$ = 1.01302. With the NaOH, aq., h varied at first somewhat irregularly but then tended to decrease; there is noticeable solution of the aniline into the NaOH, aq., but the density changes were not determined.

(23) *Chlorobenzene*, from the British Drug Houses Ltd., was fractionated and the samples 23a and 23b were obtained. The latter was probably the purer; it was twice the bulk of sample 23a; both gave with water solutions very feebly acid, and after 20 hours contact with water at 30° sample 23b gave an acid solution. For both samples and water the rise of h with time rather more than counterbalanced the decrease of (d—d′). The rise of I.T. might be due to the increasing acidity of the solution next the capillary meniscus.

(24) *Benzyl chloride* was distilled and about half of the original liquid was obtained as samples 24a and 24b. These were nearly but not quite clear and colorless; on shaking with water for a minute these samples gave no decided acid solutions; after being in the I.T. apparatus for 4 days, the water therefrom was acid, containing HCl but in no great amount. In the I.T. experiments in the initial settings h was constant; thereafter h decreased with both samples, and approximately proportionately to the time and showing no signs of reaching a limit; the rate of decrease was somewhat greater for sample 24a. In both experiments the benzyl chloride became quite opalescent or turbid. The turbidity began a few minutes after the contact with water, was pronounced throughout the oil after one hour, was always most prominent at the outer meniscus, and was somewhat more marked with sample 24a than with 24b, and with the latter sample was not worse (perhaps better i.e. thinner) during the last two days than it had been during the first two days. This turbidity was therefore due to the solution of the water in the oil mainly, but hydrolysis had undoubtedly occurred to some extent and might have been partly responsible for the turbidity as for the decrease in the I.T. The benzyl chloride, after drying with $CaCl_2$ and filtering, had $D_{4°}^{13°}$ = 1.1050 and at 13° its S.T. = 38.3 dy/cm; therefore the maximum I.T. against water at 13° would be 73.9 − 38.3 or 35.6 dynes/cm. As the initial I.T. at 30° was 30 dynes/cm, the mutual solubility was not large. On contact with a concentrated salt solution at 30° the benzyl chloride immediately gave such a turbidity that the menisci could not be seen and therefore the I.T. could not be determined.

(25) *Ethyl acetate, sample 25*, was that as supplied by Merck. The greater portion was washed several times with water and all of the water washes were acid. Then it was shaken for some minutes with $CaCl_2$, filtered on to K_2CO_3. After 40 hours it was filtered on to P_2O_5, shaken therewith for 1 hour, filtered off and then slowly fractionated. Rejecting the first quarter, there were collected the samples 25a and 25b, each in bulk about a third of

the original liquid. Sample 25b appeared to be very pure product (see previous paper); on shaking with water for a minute at the ordinary temperature it gave a neutral solution, but that from the I.T. test after 49 hours was acid. With ethyl acetate and water the solubility and density changes are too great to allow the study of the effect of the hydrolysis, if any, on the I.T. with water. With the sample 25a and a concentrated salt solution the I.T. was greater and its variations were less than with water; after the test the salt solution was neutral. With the sample 25b and the N. HCl, aq. the value of h decreased with time and became zero after 18 hours; as (d — d′) also decreased with time, the I.T. decreased faster than h did. With the NaOH, aq. h decreased more slowly, at any rate after the first few hours. With the acid and the alkali solutions it may be considered that the hydrolysis is affecting the I.Ts.

(26) *Butyl acetate*, from W. J. Bush and Co., London, was dried with K_2CO_3 for 18 hours and then fractionated. The first tenth, b.p. 118°-120°, was neglected; then samples 26 a, b, and c were collected, in bulk about one-eighth, one-half and one-fourth of the original liquid. With sample 26b the rate of increase of the b.p. was the least. These fractions are undoubtedly mixtures, probably of the normal primary and secondary butyl acetates. These samples with water gave slightly acid solutions. The water from the I.T. test with 26b, after 140 hours contact at 30°, was still feebly acid. On boiling for a minute or on keeping the ester and water together for a month at the ordinary temperature the acidity increased. Sample 26a would be the least pure; it probably contained a trace of alcohol, the smell of which was noticed in the preceding, discarded fraction; the variation in the I.T. was the greatest for this sample. With the N HCl, aq. the butyl acetate, 26b, gave h constant in the first three settings over four hours. The fourth setting was observed over 10 days, for the middle 7 days of which, however, the temperature was about 12° and not 30°. In this setting h decreased but the rate of decrease became very slow after the second day. The "final I.T." in Table III (Series X) was that obtaining after 24 hours, which will be more comparable with the final I.Ts. given for the other oils. After the 10 days the I.T. was 5.33 dy/cm, a reduction of 30% from the initial value. No turbidity or irregularity was noticed in this test. With the N NaOH and sample 26b, in the third setting h decreased continuously, the rate of decrease being just less than that with the N. HCl over the same period.

(27) The *amyl acetate* was that purified in 1922, but in the present experiments two fractions of the material were worked with; the sample used in 1922 was the first fraction, 27a, and the next fraction was sample 27b. Sample 27b gave with water a feebly acid solution and the water after the I.T. test was definitely acid; probably sample 27a would be similar. Sample 27b was optically inactive, while 27a was slightly dextro-rotatory. For 27a and water the I.T. was recalculated from the 1922 data. The density of sample 27a was re-determined at 30° and found to have increased from 0.8545 in 1922 to 0.8554 in 1924. With this substance and the acid and alkali solutions h and (d-d′)

decreased together and thus the I.Ts. decreased. With the NaOH, aq. the first setting gave the initial I.T. given in Table III; for the next hour the I.T. was constant at 11.80, and then decreased.

(28) *Ethyl butyrate*, from W. J. Bush and Co., was treated with K_2CO_3 for 17 hours, then filtered and fractionated. The first fraction, b.p. 81.5°-112.5°, about five-ninths of the original, was further purified; the second fraction was used as sample 28c and the third fraction as sample 28d. 28c was two-ninths and 28c was one-ninth of the original. The above first fraction was washed with water, dried for 5 days over K_2CO_3 and again fractionated, when it gave one quarter of b.p. 101°-104.5°, which was neglected, one quarter as sample 28a and the third quarter as sample 28b. Perkin (loc. cit) gives for ethyl n.-butyrate the b.p. = 121.2° and $D^{30°}_{4°}$ = 0.8680 and for ethyl isobutyrate the b.p. 110.2° and $D^{30°}_{4°}$ = 0.8588. Our samples 28a-d had decreasing densities and increasing boiling points, and they must be somewhat complex mixtures containing probably methyl and ethyl normal and isobutyrates. (The original ethyl butyrate, and butyl acetate were optically inactive.) Samples 28c and 28d with water gave feebly acid solutions, and the waters from the I.T. tests with 28a and 28b were feebly acid but after keeping for a month with the ester became definitely acid. With this substance and water the I.T. was constant, but with the N. HCl, aq. the I.T. decreased continuously—the two experiments agreeing well. With the N. NaOH the I.T. decreased rapidly at first, and then slowly; the initial I.T. may be as high as 13.7 dy/cm.

(29) *Amyl butyrate*, from W. J. Bush and Co., a slightly yellowish liquid, was used as sample 29; it had $D^{13°}_{4°}$ = 0.8725 and $[\alpha]^{13°}_{D}$ = + 0.80°. The greater part was distilled, giving one-sixth of b.p. 152°-166°, which was neglected, and then samples 29a, 29b and 29c, in bulk about one-third, one-fourth and one-sixth respectively of the original liquid. The distillates were colorless; they gave with water neutral solutions, becoming feebly acid after standing awhile and after a month's contact definitely acid. After the I.T. tests the waters were feebly acid. All of these liquids are, of course, mixtures of various isomers. With the N NaOH, aq. h tended to increase in successive settings, diminishing in each setting, and behaving as if there was a film hindering the motion of the capillary meniscus; no film was visible. This behaviour was also given in liquid 30b; with liquids 33, 34, 35, 37, 38 and 39 the filming or turbidity was visible and contamination of the meniscus was quite evident.

(30) *Amyl valerianate*, from W. J. Bush and Co., was a yellow liquid; it had $D^{13°}_{4°}$ = 0.8772 and $[\alpha]^{13°}_{D}$ = + 0.67°. Part was filtered and used as sample 30. The greater part was distilled; the first distillate boiled from 100° to 171.5°, formed about 6 per cent of the original and was neglected; then were collected the samples 30a, 30b and 30c, in bulk about 24, 30 and 18 per cent respectively of the original liquid. These liquids, too, are obviously mixtures of isomers and related compounds. The boiling point of iso-amyl iso-valerate is given as 189°-190° in Atack's Year Book. These samples gave with water acid solutions. With the N NaOH, aq. this substance behaved similarly to the amyl butyrate (q.v.); after these tests the NaOH, aq. was yellow colored.

(31) *"Oenanthic ether"*, from Merck, was shaken for a short time with $CaCl_2$,—long contact resulted in some combination, as is the case with several esters, e.g. ethyl, butyl and amyl acetates. The liquid was then filtered off and distilled; a little came off at about 80° and then the temperature rose rapidly to above 200°. After discarding a small amount, the samples 31a and 31b were collected. This material, according to Roscoe and Schorlemmer, is a mixture of the ethyl esters of several fatty acids, especially caprylic, pelargonic and capric acids; it would not contain much, if any, of ethyl oenanthate. Both samples 31a and 31b gave with water acid solutions. With NaOH, aq. they gave immediately a thick white solid or soap, so that this I.T. could not be determined.

(32) *Benzyl acetate*, from W. J. Bush and Co., was distilled; the first fraction, about 15 per cent of the original, b.p. = 212.5°-214°, was discarded, and then were collected the samples 32a and 32b, about 35 and 28 per cent respectively of the original liquid. These with water gave feebly acid solutions, sample 32a giving the greater acidity.

(33) *Methyl benzoate*, from L. Givaudan and Co., was distilled; the first distillate, one quarter, was discarded, and then was collected sample 33,—in bulk one-half of the original. Sample 33 gave with water a very feebly acid solution, and after the I.T. test of 65 hours the water was no more acid. With this sample and the N NaOH, aq. h decreased continuously, so that the initial and final I.Ts. were taken from the h—time graph. Here turbidity was noticed at the interfaces and in the ester.

(34) *Isobutyl benzoate*, from L. Givaudan and Co., was distilled; the first sixth was discarded and then was collected sample 34, about two-thirds of the original bulk. The sample gave with water a feebly acid solution and was probably a little worse in this respect than the original liquid. This liquid is heavier than water at room temperature (about 12°), but the liquid at 30° is lighter than water at 30°. The value of $(d - d')$ at 30° is so small that in our apparatus the I.T. with water could not be determined as a large enough value of h could not be accommodated. This substance was optically inactive. From the I.T. against salt solution the I.T. against water was reckoned as 24.1 dynes/cm (maximum value) at 30°. There was marked turbidity with the NaOH, aq.

(35) The purest *benzyl benzoate*, from W. J. Bush and Co., was a colorless, odorless, viscous liquid. Part was filtered only and formed the sample 35. Part was distilled; the first fraction, one-ninth, was discarded, and then was collected sample 35a, about two-thirds of the original bulk. The liquid during distillation developed a yellow colour and a slight odour (of benzaldehyde ?); sample 35a was very slightly yellowish and practically odorless. The sample 35 with water gave a slightly acid solution and sample 35a a distinctly acid solution. Evidently therefore there was a little decomposition during the distillation. The waters from the I.T. tests were feebly acid to litmus. With water the I.T. decreased with time and faster with sample 35 than with sample 35a; turbidity in the apparatus was marked with 35 and very slight with 35a. With the NaOH, aq. there was turbidity etc.

(36) *Methyl salicylate* was shaken with a little anhydrous K_2CO_3, filtered and distilled; after discarding the first distillate, the sample 36 was collected. (Atack's Year Book gives the b.p. as 224°). With water it gave a feebly acid solution.

(37) *Amyl salicylate*, from L. Givaudan and Co., was a colorless, somewhat viscous, fragrant liquid. It boiled at a high temperature with a little decomposition. This liquid therefore was used as supplied; it had $D_4^{13°} = 1.0569$ and $[\alpha]_D^{13°} = +1.82°$; with water it gave a neutral solution. After the I.T. test of 48 hours the water was very feebly acid. With the H_2SO_4, aq. h decreased rapidly and continuously. With the N NaOH, aq. a milky soapy mass was formed in a few seconds and the I.T. could not be determined.

(38) *Ethyl phthalate* was supplied by L. Givaudan and Co., as "Neantine"; it was a clear colorless viscous liquid. It was not certain whether this material is the acid ester (mono-ethyl phthalate) or the neutral ester (di-ethyl phthalate). It was distilled under reduced pressure and the first third was collected as sample 38, the b.p. being constant. This sample was not appreciably soluble in water, though the solution became acid in a few minutes. With the N NaOH, aq. turbidity and contamination of the meniscus were marked.

(39) *Ethyl acetoacetate*, from Kahlbaum, a straw-colored liquid, was distilled. After rejecting about one-fifth, there was collected over one-half of the original liquid as sample 39. This sample was used with water, a salt solution and the N NaOH, aq. The used material was separated, dried with $CaCl_2$ and re-distilled giving sample 39′. This was slightly straw-colored, the distillation being carried rather far. Sample 39′ was used with water and the H_2SO_4, aq. With water the two samples gave an acid solution, the acidity increasing with the time of contact; also the mutual solubility was considerable and the density changes were marked. Our samples were not of the highest purity, but only a limited supply of material was available. Perkin gives for ethyl acetoacetate the b.p. = 180°-182° and $D_{4°}^{30°} = 1.01501$. The density given in Table I for sample 39 may be low; a second determination a fortnight later gave $D_{4°}^{30°} = 1.01474$. The value 1.01460 was taken in the tests with sample 39 and the salt and soda solutions. But perhaps the density of this substance increases with time, owing to changes (v. Table V). In the I.T. tests with water the value of h decreased continuously; considering the variations possible, the two tests agreed quite well. After 12 hours h did not decrease much, giving then a minimum I.T. of about 3 dynes/cm. With the salt solution the I.T. decreased very slowly; solubility differences might explain the differences between the latter test and the I.T. tests with water, but decreased hydrolysis probably helps the explanation. With the H_2SO_4, aq. h decreased rapidly for 20 hours, then less rapidly for the next 20 hours, and then more rapidly than ever. After 20 hours bubbles of gas were noticed rising from the acid solution, and after 40 hours they were continuously rising and passing up through the acid solution, the outer meniscus and the ethyl acetoacetate; the gas was carbon dioxide. The density of the acid solution from this I.T. test could not be determined by the S.G. bottle on account of

the gas evolution, and the approximate value thereof was assumed from the experiment with water. Evidently ketonic hydrolysis (the products being acetone, alcohol and CO_2) was proceeding with the ethyl acetoacetate dissolved in the sulphuric acid solution. The presence of the first two products of the hydrolysis would undoubtedly cause a lowering of the I.T. With the NaOH, aq. turbidity developed immediately after contact and made it impossible to obtain readings of h after 40 minutes; during this time the I.T. was constant (but no corrections were made for mutual solubility etc.).

(40) *Maize oil, sample 40,* is that of 1922, which was used as supplied; see the previous paper, from which the results are quoted. In 1924 it was filtered and re-investigated as *sample* 40 *a*; here too with water the menisci became flatter and turbidity developed in the oil with time,—after half an hour the outer meniscus was appreciably flatter and after several hours it was contaminated and crinkled. Sample 40a had lighter I.Ts. with water than sample 40 at corresponding times and perhaps a somewhat lower rate of decrease of I.T.

Maize oil, sample 40′, was from a different source. It filtered hot to a clear yellow liquid—lighter than samples 40 and 40a. In the I.T. test with water turbidity was noticeable at the outer meniscus only after some 6 hours. The low I.T. and rapid decrease of I.T. of oils like 40, 40a and the 1922 fatty oils might be due partly to colloidal impurities therein, as well as to hydrolysis by water.

(41) *Cotton Seed oil* after filtering was an orange yellow liquid, sample 41. With water turbidity was noticed after 5 hours, and the menisci behaved as if contaminated.

(42) *Sperm oil* was filtered cold (at 10°) from some dark and whitish sediment and gave *sample 42*, a clear light brown oil with a slight greenish fluorescence. After keeping at room temperatures, 10° and less, for a month, the sample had deposited more yellowish solid, stearin or spermaceti. *Sample 42a* was thus prepared by placing sample 42 in a freezing mixture at −8° for an hour and then putting the semi-solid mass on a filter-paper and letting it drain at about +8° for 5 hours; the filtrate, sample 42a was a little over half the bulk of the original oil, which it closely resembled. The I.Ts. of these samples with water decreased with time; no turbidity was noticed with sample 42 and very little with sample 42a; in both cases the outer meniscus became flatter with time. The final water from the I.T. test with 42a was neutral. A short first setting with sample 42 gave the I.T. of 4.48 dy/cm, constant over half an hour; this value was neglected in Tables I and IV.

Summary

There have been measured the interfacial tensions of organic liquids against water and aqueous solutions at 30°, and also the densities of the mutually saturated solutions. In addition, the variations of these interfacial tensions with time were observed over long periods. When two partially miscible liquids saturate each other, their densities usually change in the normal manner, i.e. the lighter liquid becomes denser and the heavier liquid less dense.

Making allowance for such density changes, there has been shown the constancy of the interfacial tension over several days between many pairs of liquids. Purification of an organic liquid tends to make its interfacial tension against water (etc.) higher and less variable with time. But many mixtures of organic liquids have with water (etc.) interfacial tensions constant over a long period; certain impurities, however, may greatly influence the interfacial tension, usually causing it to decrease continuously with the time of contact.

The greater the mutual solubility between two liquids, the lower is the interfacial tension between them, i.e. between their saturated solutions. With certain esters and dilute acid and alkali solutions in water the interfacial tensions decrease largely with the time. Here the varying interfacial tension is due to the hydrolysis of the esters, when the products of the hydrolysis increase the mutual solubility of the two liquids or give a contaminated interface between them. The detailed summary is in § (1) to (15), pp. 7 to 11.

In conclusion the writer desires to thank Messrs. N. Brelaz, G. Cornwell, W. Davies and G. Harker, and also Jas. Hardie and Co., Melbourne, for donations of organic liquids and oils.

The School of Mines,
Ballarat.
December, 1925.

HEATS OF ADSORPTION AND THE PROBLEM OF PROMOTER ACTION*

BY CHARLES FREDERICK FRYLING[1]

The heat of adsorption of hydrogen on catalytic nickel has recently been measured by Foresti[2], who obtained values at variance with those of Beebe and Taylor[3]. Both of the methods employed were apparently of the same order of accuracy, and the fact that neither of the above results agreed with those obtained in this investigation, shows that the problem is less simple than it was first thought to be.

Recent work has thrown considerable light on the role of promoters in the surface of contact agents. Thus, Russell and Taylor[4] have shown that thoria in a nickel catalyst prevents coalescence of the unsaturated nickel surface atoms. Wyckoff and Crittenden[5] have confirmed this conception by a thorough X-ray examination of promoted ammonia catalysts. Since adsorption has been shown to be so intimately connected with catalytic activity,[6] it was thought that a study of the (probably enhanced) thermal effects occurring with adsorption on promoted catalysts might reveal the nature of the change produced in the adsorbed gas whereby its chemical activity is increased.

Measurement of the Heat of Adsorption.—The method of Beebe and Taylor (q.v.) was used. These authors found a troublesome adsorption drift with nickel catalysts. The effects of this were largely overcome by taking the temperature readings for ten minutes instead of three minutes. This necessitated an accurate knowledge of the cooling curve. It was found that the calorimeter cooled according to Newton's cooling law. The linear relationship between the rate of cooling and the temperature facilitated this correction. Consequently, temperature readings were taken every half minute, and the total cooling correction was the sum of the half-minute corrections. The accuracy of this procedure was about two per cent. Furthermore, it was found that the rate of cooling was not influenced by the amount of catalyst within the calorimeter, nor by the volume or nature of gas present so long as 2 c.c. of nitrogen were present.

The temperature of evacuation of the catalyst was 300°C. for all cases, with the exception of those presented in Table IV, which were evacuated at 0°C. All of the heats of adsorption were measured at 0°C.

It was important to determine the heats of adsorption at low pressures. Small amounts of gas were admitted into the calorimeter, and the heats of adsorption at constant volume (Q_v) were measured. When values for the heats of adsorption of the total amount of gas adsorbed were obtained, since the pressure was kept constant, they were designated as (Q_p). Following the procedure of Foresti, this value was diminished by 0.5 kg.-cal. to make it comparable with the measurements at low pressures.

---

* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] National Research Fellow in Chemistry.

[2] B. Foresti: Gazz. 53, 487 (1923); 55, 185 (1925).

[3] Beebe and Taylor: J. Am. Chem. Soc., 46, 43 (1924).

[4] Russell and Taylor: J. Phys. Chem., 29, 1325 (1925).

[5] Wyckoff and Crittenden: J. Am. Chem. Soc., 47, 2866 (1925).

[6] Hugh S. Taylor: "Colloid Symposium Monograph", (1923).

The method of Beebe and Taylor has been found to give measurements with an a.d. of 3% for total adsorption. From this it has been calculated that the a.d. rises to about 20% for 0.6 c.c. of gas adsorbed, 10% for 1 c.c., 6% for 2 c.c., and 4% for 4 c.c. However, for values obtained in sequence, the deviations were not so marked as these figures indicate. But little value was accorded to the absolute values recorded, the variation of the heat of adsorption with amount adsorbed being deemed of greater significance. A source of error was introduced by a slight adsorption (ca. 0.6 c.c.) of nitrogen on the promoted catalysts. It was considered a possibility that this was responsible for the interesting variation obtained in these cases; but, several determinations made on the promoted catalysts without nitrogen present, showed that such could not be the explanation.

Preparation and Purification of Gases.—The gases were prepared and purified by the same methods used by Russell and Taylor. It was found, however, that carbon dioxide prepared from marble contained a small residue (ca. 1%) of gas which would not dissolve in sodium hydroxide solution. This may explain the poor results obtained with this gas, since it was determined that a small amount of air admitted with hydrogen gave an abnormally high heat effect. Such being the case, extreme precautions were necessary relative to the purity of the nitrogen and hydrogen employed.

Preparation and Catalysts.—Recrystallized C.P. nickel nitrate was used for catalysts I, II, and III. Pure metallic nickel, dissolved in C.P. nitric acid, was the basis of catalysts IV, V, and VII. Merck's commercial nickel carbonate was used for catalyst VI. At first the catalysts were ignited in a porcelain casserole to expel the oxides of nitrogen; but it was later found that better results could be obtained if the nitric acid solution of nickel was ignited in a large Pyrex test tube in a tubular electric furnace. A glass tube was inserted into the upper part of the test tube, and suction from a water pump removed the gases and steam evolved. As the solution evaporated, the temperature of the furnace was raised slowly enough to prevent foaming and excess spattering until 300°C. was reached. This procedure seemed to incorporate the promoter more thoroughly with the nickel oxide. The oxide was then transferred to a Pyrex glass furnace of the type described by Rideal and Taylor[1] and reduced at 300°C. with hydrogen. C.P. cerium nitrate and thorium nitrate were employed as promoters. These reagents were tested and found to be free from sulphates.

Table I gives the necessary data relative to the various catalysts employed. It was deemed significant that no highly adsorptive catalysts of the type prepared by Foresti or Schmidt[1] were obtained. Catalyst III was prepared according to Foresti's directions. A very pronounced shrinkage was observed when the oxide, obtained from nickel carbonate, was reduced. Indeed, it occurred even after the catalyst had been transferred to the calorimeter, and it eventually rendered it impossible to obtain concordant values for the heat effect. It is believed possible that both Schmidt and Foresti had some impurity in their nickel carbonate which acted as a promoter and prevented coalescence of the nickel particles, for catalyst VII, which contained thoria to the amount of 13.5% of the nickel present, underwent no appreciable shrinkage when reduced from the oxide.

---

[1] Rideal and Taylor: "Catalysis in Theory and Practice", 72 (1919).

The amount of promoter in Table I is calculated as per cent of nickel present in the nickel nitrate. Catalyst I, although promoted, did not act as such. The promoter was evidently not incorporated well enough with the nickel. The fact that the best catalysts were jet-black, as noted by previous investigators, was confirmed in all cases with the exception of catalyst VII. An excess of promoter was used in the preparation of this catalyst and it is thought that finely divided thoria,.on the surface of the nickel, was the cause of this exception.

Results.—Table II presents the values of the integral heat of adsorption for varying amounts of hydrogen adsorbed. The Roman numerals designate the catalyst employed. The heats of adsorption are given in kg.-cal. per g. mol of hydrogen adsorbed.

Table III presents the values obtained for the integral heats of adsorption of carbon dioxide on nickel catalysts. It seemed evident that the values ob-

TABLE I

Catalyst number	weight g.	Cc. of H_2 adsorbed at 760 mm. by 100 g.Ni	Preparation
I	21.5	97.3	4% Ce_2O_3 Reduced from oxide at 300-320° for 260 hours.
II-a	27.0	32.6	Reduced from oxide at 300-320° for 260 hours.
II-b	"	30.7	Accidentally poisoned.
II-c	"	11.6	Sintered for 14 hours at 450°.
III	25.6	77.4	Reduced from nickel carbonate according to Foresti, for 72 hours at 300-320°.
IV-a	20.4	71.1	6.4% ThO_2. Reduced for 72 hours at 300-320°.
IV-b	"	20.5	Sintered at 400° for 20 hours.
V	21.9	?	Identical with IV-a.
VI	33.3	90	Reduced from com. nickel carbonate at 300-320° for 120 hours.
VII	23.2	71.9	13.5% ThO_2. Reduced at 300-320° for 60 hours.

Schmidt: Z. physik. Chem., **118**, 193 (1925).

TABLE II

Integral Heats of Adsorptions of Hydrogen on Nickel Catalysts

I		II-a		II-b		II-c		III	
Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v
0.21	19.7?	2.17	18.1	0.42	28.7	1.29	12.2	1.08	25.6
1.83	29.2	2.48	15.6	0.84	24.8	2.28	9.1	1.27	38.8?
1.85	28.8	2.74	14.3	2.01	16.4	3.14	7.4	7.12	14.5
2.02	24.5	3.12	12.4	4.43	12.5			18.4	10.0
2.99	22.4	4.35	10.6	5.09	12.0			19.8	9.4
4.04	16.9	8.03	11.0	7.80	10.1				
6.23	14.6	8.21	10.5	8.29	10.2				
16.7	10.2	8.81	10.1						
18.2	9.9								
19.3	10.8								
19.6	10.0								
20.3	9.9								
20.6	9.8								
20.9	9.4								

TABLE II (continued)

IV-a		IV-b		V		VI		VII	
Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v
0.61	11.3	0.76	27.6	0.83	17.5	1.32	25.6	0.72	ca 15
1.40	18.7	1.38	22.1	1.75	25.0	2.57	21.4	0.73	13.5
1.71	21.1	1.98	16.3	2.41	27.2	3.81	19.6	1.42	20.3
2.08	23.2	2.98	16.9			6.00	17.7	1.48	ca 22
2.45	25.8	4.18	15.1			8.66	16.3	2.13	24.4
2.65	25.5					26.5	13.6	2.81	25.8
3.62	22.6							4.83	26.1
5.21	19.0							5.69	25.4
10.9	16.0							7.70	21.9
11.6	15.5							16.7	16.3
14.0	16.2								
14.5	15.7								

TABLE III

Integral Heats of Adsorption of Carbon Dioxide on Nickel Catalysts

I				II-b			
Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v	Cc. ads.	Q_v
1.77	17.6	15.6	6.6	0.43	9.3	3.78	7.3
13.3	9.0	18.8	7.6	2.63	7.1	4.00	5.4

TABLE IV

Integral Heats of Adsorption of Hydrogen on Catalyst II-a evacuated at 0°C.

Cc. ads.	Q_v	Cc. ads.	Q_v
1.93	8.9	2.43	8.8
4.91	9.6	4.51	8.7

Av. = 9.0 a.d. = 0.3

TABLE V

Differential Heats of Adsorption of Hydrogen on Nickel

Cc. previously adsorbed	Cc. ads.	Value plotted	Corrected temp. rise	calories evolved	cal./Cc. adsorbed	kg.-cal./g. mol adsorbed
			Catalyst VI	Calibration = 10.4 cal/°C.		
0	1.32	0.66	0.145	1.508	1.14	25.6
1.32	1.25	1.95	0.091	0.947	0.76	17.0
2.57	1.24	3.19	0.084	0.874	0.70	15.8
3.81	2.19	4.91	0.135	1.404	0.641	14.4
6.00	2.66	7.33	0.152	1.581	0.595	13.3
8.66	17.8	17.56	0.944	9.82	0.559	12.4
			Catalyst VII	Calibration = 9.92 cal./°C.		
0	0.73	0.37	0.045	0.446	0.611	13.7
0.73	0.69	1.08	0.085	0.843	1.222	27.3
1.42	0.71	1.78	0.104	1.032	1.453	32.5
2.13	0.68	2.47	0.092	0.912	1.331	29.8
2.81	2.02	3.92	0.241	2.390	1.183	26.5
4.83	0.86	5.26	0.084	0.833	0.959	21.5
5.69	2.01	6.70	0.108	1.072	0.533	11.9
7.70	9.04	12.22	0.467	4.63	0.512	11.5

tained for hydrogen were of greater importance, so the work on carbon dioxide was discontinued.

In Table IV are a few values of the integral heats of adsorption on catalyst II-a when evacuated at 0°C.

Table V presents the values of the differential heats of adsorption of hydrogen on two typical catalysts, VI and VII.

Discussion of the Results

H. S. Taylor[1] has proposed a theory of the catalytic surface based on the results of modern X-ray methods of analysis of crystal structure. In the "Fourth Report of the Committee on Contact Catalysis",[2] he has successfully treated the whole subject with the aid of this conception. Briefly stated atoms of varying degrees of saturation are to be found in the catalytic surface. To the most unsaturated of these atoms is to be ascribed catalytic activity. The following quotation from the latter report, with reference to catalytic nickel, is most apt. "There will be a certain variability in the surface fields of attraction with variation in the exposed faces. The fields will be weakest in the closest packed faces, i.e. the 111 faces, stronger in the 100 faces and strongest in the 110 faces. Atoms in the edges of such a crystal will be one degree less saturated than the atoms in the surfaces". An atom within the crystal may be considered as having six bonds, analogous to valence bonds.

---

[1] H. S. Taylor: Proc. Roy. Soc., **108A**, 105 (1925).

[2] Taylor: J. Phys. Chem., **30**, 145 (1926).

Varying degrees of unsaturation are exhibited according to the number of free bonds. Thus a singly attached nickel atom is the most unsaturated and, according to this theory, exhibits the greatest catalytic activity.

Before it is possible to treat the measurements made in this investigation in terms of this theory, it is necessary to make one additional assumption, namely, that active nickel atoms dissociate hydrogen molecules. This assumption, however, can be logically deduced from the probable properties of the most unsaturated surface atoms. These atoms are in an almost gaseous condition, in short, they are in a state corresponding to a higher temperature than are the rest of the nickel atoms. They are analogous to Christiansen's "hot molecules" in that they possess large amounts of potential energy. To deduce this assumption, it is only necessary to consider the influence of hot metals on hydrogen.

Langmuir[1] found that tungsten, at high temperatures, dissociates hydrogen. Sieverts[2] found that nickel dissolves hydrogen at temperatures above 300°C., and from the fact that the solubility of hydrogen varies as the square root of the pressure, he concluded that the dissolved hydrogen is in the atomic condition. This same relationship holds for other combinations of gases and metals, and McKeehan[3] has shown by X-ray analysis that hydrogen probably exists as atoms in palladium.

Further evidence in favor of the existence of atomic hydrogen on the surface of catalytic nickel is furnished by the studies of the critical potentials of hydrogen in the presence of nickel catalysts by Gauger[4] and by Wolfenden[5]. It is believed that these considerations, together with the evidence found in this investigation, constitute sufficient proof for the validity of the assumption that un-ionized atomic hydrogen, of the type produced by Langmuir, Wood[6] and Bonhoeffer[7] exists on the surface of hydrogenating catalysts.

Total Adsorption.—In agreement with Russell and Taylor, it may be seen from Table I that the total adsorption is not an absolute criterion of catalytic activity. The promoter may not change the adsorptive capacities of the catalysts to any great extent; although it is conceivable that, by the proper choice of promoter and method of preparation, nickel catalysts, possessing adsorptive capacities in excess of any hitherto recorded, may be prepared. Kubota and Yoshikawa[8] in an interesting study of selective poisoning of nickel catalysts, present results which tend to show that 62% of the nickel atoms are in the surface. From the data of Table I, it can be calculated that not more than 0.2% of the nickel atoms are capable of adsorbing hydrogen. Thus, it would seem that only a small fraction of the surface is covered with hydrogen. However, it is very improbable that so high a percentage of the nickel atoms exist in the surface. It is likely that the reagent (hydrogen sulphide) employed reacted with more than surface atoms. An infallible criterion whereby the total percentage of molecules in the surface of a catalyst might be determined, would be of great advantage. The experimental results obtained by the above authors are in complete agreement with the requirements of Taylor's theory, although they do not so interpret them.

---

[1] Langmuir: J. Am. Chem. Soc., **37**, 417 (1915); **38**, 1145 (1916).
[2] Sieverts: Z. Elektrochem , **16**, 707 (1910).
[3] McKeehan: Phys. Rev. **21**, 334 (1923).
[4] Gauger: J. Am. Chem. Soc., **46**, 674 (1924).
[5] Wolfenden: Proc. Roy. Soc., **110A**, 464 (1926).
[6] Wood: Proc. Roy. Soc., **97A**, 455 (1921).
[7] Bonhoeffer: Z. physik. Chem., **113**, 199 (1924).
[8] Kubota and Yoshikawa: Sci. Papers Inst. Phys. Chem. Research, **3**, 223 (1925).

Effect of Heat Treatment of Catalysts.—Taylor and Beebe found that heating a nickel catalyst for 21 hours at 450°C. reduced its adsorptive capacity from 17 cc. to 8 c.. and increased the total integral heat of adsorption from 14.2 kg.-cal. to 20.7 kg.-cal. In another case, these authors, by heating a nickel catalyst for 4 hours at 450°C. reduced its adsorptive capacity from 35 cc. to 16 cc. and increased the heat of adsorption from 13.5 kg.-cal. to 15.5 kg.-cal. Foresti thought these results to be contrary to the theory of active centers and, upon duplicating the heat treatment of the above authors, he found a decrease in the integral heat of adsorption from 15.2 kg.-cal. to 14.5 kg.-cal.

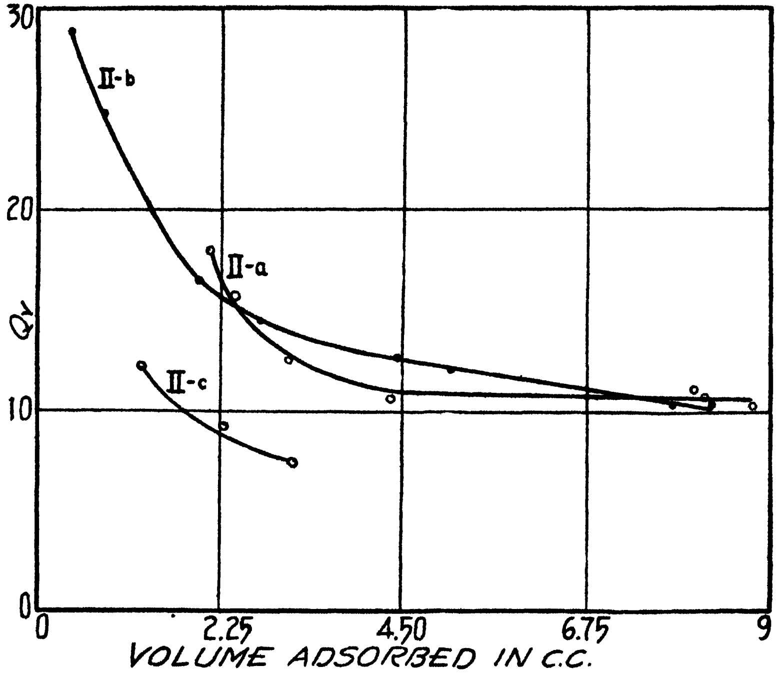


FIG. 1
Integral Heats of Adsorption of H_2 on Ni in kg.-cal. on Catalyst II

From Table II and Fig. 1 it may be seen that the heat treatment of catalyst II-a reduces the values of both the adsorptive capacity and the total integral heat of adsorption, the former from 8.81 cc. to 3.14 cc. (the saturation capacity of II-c) and the latter from 10.1 kg.-cal. to 7.4 kg.-cal. In the case of the promoted catalyst IV-a, heat treatment reduced the adsorptive capacity from 14.5 cc. to 4.18 cc. and only a slight decrease (from 15.7 to 15.1) in the value of Q_v resulted.

Taylor's theory requires that heat treatment of the catalyst should lower the heat of adsorption, since the more active centers on the catalyst are destroyed by sintering. It is evident that Beebe and Taylor's results do not agree with this theory, and unless some other effect is found to explain their values, the theory will require modification. However, from the description of their catalysts, and from the values obtained for the total integral heats of adsorption, it seems likely that these authors made their measurements on accidentally promoted catalysts. The evidence in favor of dissociation of hydrogen on active nickel surface atoms permits of a formulation of these phenomena which is in complete accord with Taylor's theory. The heat of dissociation of hydrogen has been shown by Langmuir to have a value of about 90 kg.-cal. The effect of destroying the active spots, which cause this strongly endothermic reaction to take place, naturally results in an increase in the net heat of adsorption. Had their heat treatment been of a more intense nature, the heat of adsorption would have been lowered again. Foresti's results, and the results recorded in Table II are in agreement with the requirements of Taylor's theory, since there were but few active centers present in the catalysts before heat treatment. Thus, by assuming that unsaturated nickel atoms dissociate hydrogen molecules, all of the data relative to the heats of adsorption on sintered nickel catalysts are in agreement with Taylor's theory.

When the dissociation theory was advanced to explain the apparent discrepancy of these results, the possibility of obtaining a Q_v-volume curve with a maximum was foreseen. This is because the first portion of the hydrogen adsorbed goes to the active centers which cause dissociation. The complete verification of this prediction will be discussed under promoter action.

Catalytic Poisoning.—Air was accidentally admitted to catalyst II-a and V. In the case of catalyst V the ability to exhibit a maximum in the Q_v-volume curve was destroyed. Values for the poisoned II-a are listed in Table II under II-b and their curves are given in Fig. 1. This case is analogous to one observed by Beebe[1] for a copper catalyst, and the poisoning is attributed to a change in the relative numbers of different surface atoms.

Promoter Action.—The Q_v-volume curves of IV-a, V and VII exhibit maxima. Fig. 2 shows this phenomenon. It is the function of the promoter to shift the maximum to the right, and it does so by increasing the number of unsaturated nickel atoms which, in turn, dissociate hydrogen. It is believed that all of the cases investigated for both simple and promoted catalysts would exhibit a maximum in the Q_v-volume curve if the method of measurement for small quantities of hydrogen adsorbed were sufficiently exact.

These results are in agreement with the ideas recently expressed by Taylor, Russell and Taylor, and Wyckoff and Crittenden. In addition they furnish vigorous support to the validity of the dissociation theory. The deformation of adsorbed molecules, advanced by numerous investigators to account for catalytic activity, is intense enough to cause complete rupture of the molecular structure.

---

[1] R. A. Beebe: Unpublished research.

Differential Heats of Adsorption.—Volmer[1], from thermodynamic considerations, came to the conclusion that the heat of adsorption upon a uniform surface is independent of the amount of gas previously adsorbed. He correctly attributed experimental divergences to the different surfaces exhibited by adsorbents. Table IV presents the values obtained for the heats of adsorption on catalyst II-a when evacuated at 0°C., and, within the limits of accuracy of the method, they agree with the above deductions. The curve so obtained is parallel to the volume axis and asymptotic to the Q_v-volume curve obtained by evacuation at 300°C. The differential heat of adsorption is the heat evolved per unit volume of gas adsorbed for an infinitesimal increase in total adsorption. It may be expressed in calories per mol or in calories per cc. of gas adsorbed, and it is only possible to measure this value approximately. By allowing sufficiently small quantities of gas to adsorb at a time, however, concordant values can be obtained. Table V contains values for the differential heats of adsorption on catalysts VI and VII. All the values obtained become constant considerably before total adsorption has been attained. The values are those actually measured in obtaining a sequence of integral heats of adsorption, and they vary more widely than do the latter values.

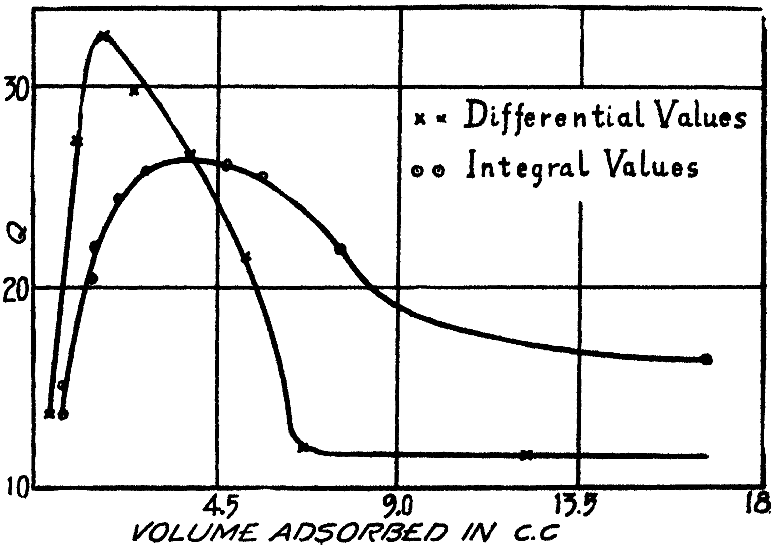


FIG. 2

Heats of Adsorption of H_2 on Ni in kg.-cal on Catalyst VII

---

[1] Volmer: Z. physik. Chem., **115**, 253 (1925).

Fig. 3 is a schematic representation of the energy relationships revealed by this investigation. The ordinate represents calories evolved per cc. of hydrogen adsorbed or differential heats of adsorption. The abscissa represents the volume of gas adsorbed. Therefore the area under the curve represents heat evolved, i.e., the integral heat of adsorption. The energy levels Q_1, Q_2, etc. represent the calories evolved when hydrogen is adsorbed on surfaces of nickel atoms of increasingly varying degrees of unsaturation. The experimental differential curve should likewise be stepwise, but an overlapping effect caused by the gas adsorbing on the atoms of lower activity before those of higher activity are fully saturated, and, in part, by impurities on the catalytic surfaces, have thus far prevented the realization of this result experimentally. The volumes V_1, V_2,—V_5 represent the number of cc. of gas adsorbed by the various types of surface atoms, and the sum of these volumes represents the adsorptive capacity of the catalyst. V_1 and V_2 are not marked on the abscissa because of lack of space. These volumes also represent the relative numbers of the different kinds of unsaturated atoms present in the catalytic surfaces. The areas FDCG, EHBF, etc. represent the integral heats of total adsorption of molecular hydrogen upon their respective types of nickel surface atom s

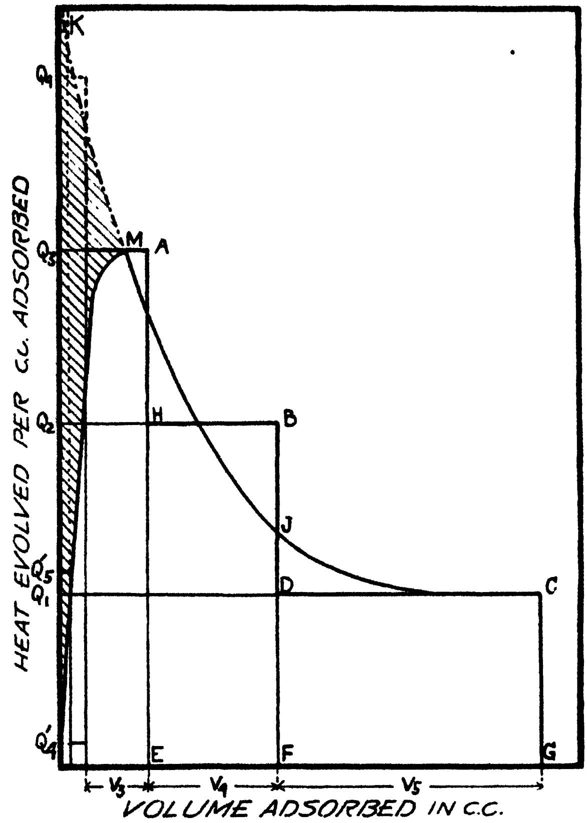


FIG. 3

In some cases the more unsaturated of these areas may be practically absent for the purpose of calorimetric determinations; consequently, curves of the type given in Fig. 1 for unpromoted catalysts will be obtained, i.e., there will be no maximum. From the discussion of total adsorption it is evident that it is not known what degree of unsaturation is required to cause adsorption. Nor is it known whether the various Q levels are even multiples of some primary value. The properties of different catalysts will be determined by the relative numbers of different types of unsaturated surface atoms present.

If no dissociation took place, the curve would follow the course K, M, J, C. Hence the shaded area represents the heat used in dissociating the gas. If this be divided by the unknown heat of dissociation of hydrogen adsorbed on nickel, the amount of dissociated gas is obtained. It is this value which is of importance in the study of reaction kinetics. Thus, by introducing a small amount of promoter into their catalyst, Russell and Taylor (q.v.) increased the reaction velocity of hydrogenation of carbon dioxide to a far greater extent than the adsorptive capacity of the catalyst. By shifting the maximum M to the right, a relatively large increase in the shaded area is produced. This area is directly proportional to the amount of dissociated hydrogen.

Q_4-Q_4' represents the unknown heat of dissociation of hydrogen adsorbed on nickel. Polanyi[1], from a study of the adsorption potential, came to the conclusion that the heat of dissociation is lowered by adsorption. Because of this uncertainty it is not known whether the Q′ levels, which represent the net heat of adsorption on the most unsaturated centers are positive or negative in value.

The value of K, the intersection of the theoretical curve with the Q axis, is of interest. If that portion of the differential curve of Fig. 2 which has the negative slope be extrapolated to the Q_v axis, values from 40 to 58 kg.-cal. are obtained. It so happens that this latter value is 5/6 of the energy estimated to be necessary to gasify metallic nickel. Therefore it is possible that the most unsaturated nickel atoms are attached to the surface by but one crystal structure bond.

Beebe and Taylor discussed the "anomalous" heat of adsorption of hydrogen on nickel when they found that there was no variation in the differential heat of adsorption. They did not extend their measurements to low enough hydrogen pressures to determine the complete nature of their integral heat of adsorption curve.

Foresti obtained values for the integral heats of adsorption of hydrogen on nickel which had been evacuated at varying temperatures up to 300°C. This procedure is equivalent to measuring the area under the curve of Fig. 3 from G to points such as F and E which are determined by the temperature of evacuation. Thus, the Q axis of Fig. 3 represents evacuation at 300°. This diagram is not drawn to scale. The area FDCG is large enough to prevent the appearance of a maximum in an integral heat of adsorption curve so obtained. From his data, Foresti calculated differential values and found that one of his samples exhibited a maximum, although he did not attribute any particular importance to the phenomenon. Thus, for evacuation within the temperature interval of 0-90°, the value of 12.2 kg.-cal. was obtained; from 120 to 145°, 19.6 kg.-cal.; and from 240 to 304°, 16.4 kg.-cal.

---

[1] Polanyi: Z. Electrochem., **27**, 142 (1921).

Conclusion

Bancroft[1] has said: "Any action between so-called saturated compounds involves either a preliminary dissociation which means the breaking of a regular bond, or a preliminary association which means the opening of a contravalence. . . . To simplify matters this problem will be discussed solely on the assumption that adsorption involves dissociation". It is evident that, in any case of hydrogenation, the hydrogen, because it is univalent, requires dissociation; although one must be careful not to consider this the sole prerequisite. In an interesting survey of the field of reactions on solid surfaces, Armstrong and Hilditch[2] in reference to this point say: "Hence, it appears that the intervention of the hydrogen is probably secondary to that of the organic compounds present, but there is still room for considerable investigation upon the precise mechanism whereby the hydrogen is brought into chemical combination". Suffice it to say, Taylor and Marshall[3] have produced a number of reactions, similar to catalytic reactions, with the aid of atomic hydrogen generated according to the method of Cario and Franck.

A number of dissociation and ionization theories[4] have been proposed, but their general application has been hindered by lack of evidence of the existence of atomic hydrogen on catalysts at ordinary temperatures and by the arbitrary assumptions regarding the dielectric constants of metals which were necessary in order to account for the energy of ionization. The present investigation has disclosed a source of energy sufficient for the purpose.

The author wishes to acknowledge his indebtedness to Professor Hugh S. Taylor for his advice, enthusiasm and criticism, and to Princeton University for its generous provision of materials, equipment and laboratory.

Summary

The heats of adsorption of hydrogen on simple and promoted nickel catalysts have been measured.

A maximum which has been attributed to the production of atomic hydrogen has been found to occur in the heat of adsorption-volume adsorbed curve for promoted catalysts.

Promoter action and the various phenomena encountered in the study of heats of adsorption have been discussed in the light of this theory and Taylor's theory of the catalytic surface.

Princeton,
New Jersey.
March, 1926

---

[1] Bancroft: Ind. Eng. Chem., **10**, 270 (1924).

[2] Armstrong and Hilditch: Chem. and Ind., **44**, 701 (1925).

[3] Taylor and Marshall: J. Phys. Chem., **29**, 1140 (1925).

[4] W. C. McC. Lewis: J. Chem. Soc., **117**, 623 (1920); Sieverts (q.v.); Polanyi (q.v.); Schmidt: Z. physik. Chem., **118**, 193 (1925).

STUDIES IN ADSORPTION. XIV

Influence of Hydrogen Ions on the Stability of Sols

BY S. GHOSH AND N. R. DHAR

In previous papers[1] we have studied the influence of hydrogen ion concentration on the coagulation of prussian blue and of arsenious sulphide sols. It has been observed that the previous addition of such acids as HCl, HNO_3 etc. makes the sols unstable towards electrolytes and quantities of KCl or KNO_3 smaller than the calculated amounts are required to coagulate the sols. On the other hand, practically additive amounts are required when the sols are coagulated with a mixture of KCl and KNO_3 or HCl and HNO_3. This marked influence of hydrogen ions on the coagulation of such hydrolysable sols as prussian blue, cupric ferrocyanide, arsenious sulphide etc. has been carefully investigated in this laboratory and an explanation of this behaviour based on the general principles of hydrolysis has been advanced.

It has already been shown in a former paper[2] that sols of the type of arsenious sulphide are hydrolysed according to the equation:—

$$As_2S_3 + 3H_2O \rightleftarrows As_2O_3 + 3H_2S$$

This hydrolysis stabilises the sol as has been observed experimentally. Now the checking of the hydrolysis by the presence of $H^\cdot$ ions will certainly render the sol unstable. The presence of OH' ions in small quantities will help the hydrolysis and make the sol more stable towards electrolytes. The results, obtained by us in a previous paper on the coagulation of arsenious sulphide sol with mixtures as KCl and $KHCO_3$, KCl and C_6H_5COONa, KCl and $NaNO_2$ and $BaCl_2$ and $NaNO_2$ etc. are of interest from this point of view because in all these cases, OH' ions are present in the mixture due to the hydrolysis of one of the electrolytes (e.g. sodium benzoate, potassium bicarbonate etc.). In Table I one set of the results is reproduced:—

TABLE I

Concentration of the sol = 0.100 grm As_2S_3 per litre. Volume = 10 c.c. Time = 1 hour. Maximum turbidity is observed.

$2NKHCO_3$ added cc.	N/2 KCl added cc.	N/2 KCl calculated cc.	Difference cc.	Percentage Difference
0	1.6	—	—	
1.9	0	—	—	
0.4	2.8	1.35	+1.45	107
0.8	1.9	0.90	+1.00	111
1.2	1.3	0.70	+0.60	86

---

[1] J. Phys. Chem., 29, 659 (1925); Kolloid-Z., 36, 129 (1925).

[2] Kolloid-Z., 36, 129 (1925).

From the results of Linder and Picton it will be seen that larger quantities of such electrolytes as potassium tartrate, potassium oxalate, potassium citrate, etc., are necessary to coagulate a sol of arsenious sulphide than that required to coagulate the same amount of the sol with KCl. Exactly similar results were obtained by us[1] in the coagulation of negatively charged ferric hydroxide, chromium hydroxide, antimony sulphide etc., when coagulated by potassium oxalate, potassium citrate, etc. This is due more to the hydrolysis of the salts of the weak organic acids than to the adsorption of the organic anions. The presence of OH′ ions due to the hydrolysis of the added electrolytes certainly stabilises the sulphide and negatively charged ferric hydroxide and chromium hydroxide sols and it is, therefore, apparent that the electrolytes, which give out OH′ ions due to their hydrolysis, are required in larger amounts than those which are not hydrolysed appreciably. We have made further experiments on this line with sols of ferric and chromic hydroxides on their coagulation by mixutres of easily hydrolysable salts and strong acids. The results are as follows:—

Ferric Hydroxide Sol

The sol was prepared according to the method of Krecke and was dialysed for a week to free it from electrolytes. The sample of sol used in these experiments was three and half months old. The experimental results are given in Tables II-IV.

TABLE II

Concentration of the sol = 1.43 gram. Fe_2O_3 per litre. Amount of sol taken each time = 2 c.c. Total volume = 6 c.c. Immediate turbidity is observed.

Coagulation with a mixture of KCl and HCl

Amount of N/100 HCl	Amount of KCl to coagulate
c.c.	c.c.
0.0	0.90 N/5 KCl
0.1	0.80 N KCl
0.2	1.20 "
0.4	1.35 "
0.6	1.30 "
0.8	1.30 "

TABLE III

Coagulation with a mixture of sodium acetate and HCl

Amount of N/100 HCl	Amount of N/20 CH_3COONa
c.c.	c.c.
0.0	0.75
0.1	1.35
0.2	1.90
0.4	2.30
0.6	2.70
0.8	3.05

---

[1] Kolloid-Z., **34**, 262 (1924); **36**, 129 (1925).

TABLE IV

Coagulation with K_2SO_4 and HCl, or $K_2C_2O_4$ and HCl

Amount of N/500 HCl	Amount of N/500 $K_2C_2O_4$	Amount of N/500 K_2SO_4
c.c.	c.c.	c.c.
0.0	0.70	0.60
0.1	0.80	0.90
0.2	0.90	1.00
0.3	0.95	1.05
0.4	1.00	1.05
0.5	1.10	1.05

Chromium Hydroxide Sol

This sol was prepared by adding ammonium hydroxide to a solution of $CrCl_3$ till the precipitate of $Cr(OH)_3$ just appeared. The sol was first dialysed for a week and then hot dialysis was continued for another week. The sol was free from acid but on dissolving the sol with HNO_3, a precipitate was obtained with $AgNO_3$ showing that chloride ion was not completely removed even by hot dialysis. The experimental results are given in Tables V-VIII.

TABLE V

Concentration of the sol = 3.91 gms of Cr_2O_3 per litre. Amount of sol taken each time = 4 c.c. Total volume = 10 c.c. Time = 1 hour.
Coagulation with K_2SO_4 or $K_2C_2O_4$ in the presence of H_2SO_4

Amount of N/100 H_2SO_4	Amount of N/500 K_2SO_4	Amount of N/500 $K_2C_2O_4$
c.c.	c.c.	c.c.
0.0	2.5	3.0
0.2	2.6	3.0
0.4	2.65	2.9
0.6	2.6	2.6
1.0	1.75	1.8

TABLE VI

Coagulation with K_2SO_4 or sodium potassium tartrate in the presence of HCl.

Amount of N/100 HCl	Amount of N/500 sodium potassium tartrate	Amount of N/500 K_2SO_4
c.c.	c.c.	c.c.
0.0	2.4	2.5
0.1	3.00	2.9
0.2	3.5	3.6
0.3	4.2	4.2

TABLE VII

Coagulation with NaCl in presence of HCl

Amount of N/100 HCl c.c.	Amount of N/10 NaCl c.c.
0.0	1.55
0.1	2.20
0.2	3.25
0.3	>4.60

TABLE VIII

Coagulation with sodium acetate in presence of HCl

Amount of N/100 HCl c.c.	Amount of N/20 CH_3COONa c.c.
0.0	0.55
0.1	0.65
0.2	0.80
0.3	0.90
0.4	1.00
0.5	1.05
0.6	1.10

Discussion

Our experimental results with ferric hydroxide and chromium hydroxide sols show clearly that the peptising influence of H$^{\cdot}$ ions is not so marked when these sols are coagulated with sodium acetate as that observed when these sols are coagulated with KCl or NaCl. Thus in the presence of 0.2 c.c. of N/100 HCl the amounts of KCl or NaCl required to bring about coagulation of ferric hydroxide sol is seven times greater than that required to coagulate the sol when no acid is present. On the other hand, in presence of 0.2 c.c. of N/100 HCl, the amount of sodium acetate required to coagulate the same sol is about 2.5 times greater than the amount necessary to coagulate the sol in the absence of acid.

In presence of 0.3 c.c. N/100 HCl with chromium hydroxide sol, the amount of NaCl necessary to coagulate the sol is three times the quantity required to coagulate the sol in the absence of the acid; whilst in presence of the same amount of acid the quantity of sodium acetate required to coagulate the same sol is 1.5 times the quantity necessary to coagulate the sol, when no acid is present.

The precipitation values of $K_2C_2O_4$ and K_2SO_4 with ferric hydroxide sol is 0.12 and 0.10 millimole per litre respectively when no acid is present. In presence of 0.1 c.c. N/500 HCl, the precipitation values of $K_2C_2O_4$ become 0.13 and 0.15 millimole respectively. Hence $K_2C_2O_4$ becomes a more effective coagulant than K_2SO_4 in presence of an acid. On further increasing the concentration of acid, it is found that the precipitation value of K_2SO_4 remains constant when 0.3 or 0.4, or 0.5 c.c. of N/500 HCl is added. On the other hand the precipitation value of $K_2C_2O_4$ goes on increasing with the increase in concentration of HCl.

When chromium hydroxide sol is coagulated by mixtures of H_2SO_4 and K_2SO_4 or H_2SO_4 and $K_2C_2O_4$ we obtain some interesting results. Our experiments show that, in absence of acid, K_2SO_4 is a better coagulant than $K_2C_2O_4$ for both the hydroxide sols. This fact is difficult to explain because experimental results show under identical conditions C_2O_4'' ion is more adsorbed than SO_4'' ion. Moreover, potassium oxalate is more hydrolysed than potassium sulphate; consequently the coagulating power of an oxalate ion should be greater than that of a sulphate ion. The probable explanation of this abnormal behaviour of $K_2C_2O_4$ seems to be that $K_2C_2O_4$ is adsorbed also in the molecular condition by the sols because of the tendency of forming complex ferric oxalates or chromic oxalates.

In presence of increasing amounts of sulphuric acid the coagulating power of potassium sulphate on chromium hydroxide sol at first remains practically constant, then it increases as the concentration of sulphuric acid is increased. On the other hand the coagulating power of $K_2C_2O_4$ increases as the concentration of sulphuric acid is increased. Though the coagulating power of K_2SO_4 is greater than that of $K_2C_2O_4$ in the absence of sulphuric acid, in presence of 0.6 c.c. N/100 sulphuric acid the coagulating power of K_2SO_4 and $K_2C_2O_4$ become equal.

It will be observed from our results on chromium hydroxide sol that, in absence of acid, sodium potassium tartrate is a slightly better coagulant than potassium sulphate, but in presence of 0.1 c.c. N/100 HCl, potassium sulphate becomes a slightly better coagulant than sodium potassium tartrate.

The foregoing results can be explained from the accepted views on the dissociation of weak acids.

It is well known that sols like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc., highly adsorb $H^{\cdot}$ ions. Consequently in presence of hydrochloric acid, the positive charge on the sol will increase and much larger quantities of KCl, NaCl, etc., will be necessary to coagulate the sol. When, however, the precipitation is effected by a mixture of sodium acetate and hydrochloric acid, the stabilisation of the sol is not as marked as that obtained when they are coagulated by NaCl and HCl or KCl and HCl, because in presence of sodium acetate the free $H^{\cdot}$ ions from hydrochloric acid are more or less completely removed due to the formation of undissociated acetic acid, as acetic acid is a weak acid. Consequently a mixture of sodium acetate and hydrochloric acid behaves as undissociated acetic acid and sodium chloride and the few $H^{\cdot}$ ions that are available for adsorption by the hydroxides slightly stabilise the sols as will be seen from the experiments.

In the coagulation of chromium hydroxide sol by a mixture N/100 HC and N/500 sodium potassium tartrate we find that as the concentration of the acid is increased the concentration of sodium potassium tartrate necessary for coagulation is also increased. When HCl is added to sodium potassium tartrate the H˙ ions immediately combine with the tartrate ion forming the acid tartrate ion because the second dissociation constant[1] of tartaric acid is 5.8×10^{-5}. Hence the H˙ ions are removed more or less completely from the solution. In presence of 0.1 c.c. N/100 HCl, the amount of N/500 sodium potassium tartrate required for coagulation is 3 c.c. Now 0.1 c.c. of N/100 HCl is equivalent to 0.5 c.c. N/500 hydrogen tartrate ion, so this amount must be subtracted from the actual concentration of sodium potassium tartrate necessary for coagulation. Thus we find that really 2.5 c.c. of sodium potassium tartrate exist as such in the solution in presence of 0.1 c.c. of N/100 HCl. The amount required in coagulating the sol in the absence of the acid is only 2.4 c.c. Hence there is only a slight stabilisation when chromium hydroxide sol is coagulated with a mixture of sodium potassium tartrate and hydrochloric acid. Exactly similar results were obtained with other concentrations of acid and tartrate.

When ferric hydroxide sol is coagulated with a mixture HCl and $K_2C_2O_4$, the results show that there is hardly any stabilisation due to the adsorption of H˙ ions, because the H˙ ions are practically removed from the solution due to the formation of hydrogen oxalate ions, the second dissociation constant of oxalic acid being 3.1×10^{-5}. In other words, a mixture of HCl and $K_2C_2O_4$ behaves in a manner exactly similar to that of HCl and sodium potassium tartrate. On the other hand, when ferric hydroxide sol is coagulated by HCl and K_2SO_4 appreciable stabilisation takes place because of the adsorption of H˙ ions. When chromium hydroxide is coagulated by a mixture of H_2SO_4 and $K_2C_2O_4$, as the oxalate ion is replaced by the sulphate ion and as both these divalent ions exert similar coagulating influence, the sol is not at all appreciably stabilised, because the H˙ ions are removed as hydrogen oxalate ions.

The foregoing considerations can readily explain the results obtained in Table IX by Sen and Mehrotra[2] with chromium hydroxide sol:—

TABLE IX

Amount of N/100 HCl	Amount of N/100 K_2SO_4	Amount of N/100 $K_2C_2O_4$
0.0	2.4	3.0
0.1	2.9	3.2
0.2	3.0	3.3
0.3	3.3	3.32
0.4	3.5	3.34
0.5	3.7	3.34

There is more of stabilisation of the sol in presence of K_2SO_4 and HCl than in presence of HCl and $K_2C_2O_4$ because there are more of hydrogen ions in the first mixture than in the second.

---

[1] Compare Datta and Dhar: J. Chem. Soc., **107**, 824 (1915).

[2] Z. anorg. Chem., **142**, 345 (1925).

Linder and Picton[1] have shown that $K_2C_2O_4$ is a better coagulant for ferric hydroxide sol than K_2SO_4, whilst the results obtained by Weiser[2] and by us show that K_2SO_4 is a slightly better coagulant than $K_2C_2O_4$. It seems likely that Linder and Picton's sol was slightly acid.

From a critical consideration of the experimental results of other workers in this field we shall show in the subsequent pages that along with the hydrogen ion concentration of the medium, the adsorption of ions carrying the same charge as the sol and the degree of hydrolysis of the sols are very important factors in their stability.

In Table X the results obtained by Tartar and Gailey[3] with mastic sol are reproduced:—

TABLE X

Electrolyte	Precipitation value in milliequivalents	Amount of the acid added in milliequivalents	Hydrogen ion concentration. pH value
KCl	75	—	4.3
KCH_3COO	400	—	8.0
”	75	62.5	4.5
K_2SO_4	225	—	4.4
”	75	0.15	4.0
$K_2C_2O_4$	275	—	5.9
”	75	7.5	4.4
K_2HPO_4	100	—	4.8
”	75	13.6	4.3

From the above table the order of the precipitation values of various potassium salts is as follows:—

$$KCH_3COO > K_2C_2O_4 > K_2SO_4 > K_2HPO_4 > KCl.$$

In a previous paper[4] we have observed that a sol of mastic appreciably adsorbs an ion carrying the same charge as the sol. The great difference in the precipitation values of different electrolytes is due to two causes (1) the adsorption of anions to a different degree, and (2) the partial hydrolysis of some of these salts viz CH_3COOK, $K_2C_2O_4$ and K_2HPO_4, with the liberation of OH' ions, which certainly peptise the sol. The first cause of stabilisation has been completely overlooked by Tartar and Gailey and the influence of $H^{\cdot}$ ions has been over-emphasised. From their data it is obvious that there is practically no difference in PH value when the sol is coagulated by either KCl(pH = 4.3) or K_2SO_4(pH = 4.4) though the precipitation value of K_2SO_4 is 3 times that of KCl.

On the other hand the pH value in the case of K_2HPO_4 is 4.8 and the precipitation value is 100, whilst with K_2SO_4 these values are 4.4. and 225. If Tartar and Gailey's contention that no appreciable adsorption of ions carrying the same charge as the sol takes place, then the precipitation value of K_2SO_4 should have been smaller than that of K_2HPO_4. These results of Tartar and Gailey show that SO_4'' ion is very likely more adsorbed than HPO_4'' ion.

---

[1] J. Chem. Soc., **87**, 1926 (1905).

[2] J. Phys. Chem., **24**, 30 (1920).

[3] J. Am. Chem. Soc., **44**, 2212 (1922).

[4] J. Phys. Chem., **29**, 435 (1925).

In a recent paper Michaelis and Hirabayashi[1] have also determined the coagulating powers of HCl, HNO_3, H_2SO_4 and sulphosalicylic acid on mastic sol and their pH values at precipitating concentrations have been measured. The effect of adding LiCl, NaCl, RbCl, K_2SO_4, Na_2CO_3, $CaCl_2$ and sodium citrate in the presence of a definite amount of $H^\cdot$ ion has also been investigated. The authors have shown that the anions are not entirely without effect, as has been concluded by Tartar and Gailey.

Moreover Bradfield[2] has determined the coagulating powers of HCl, H_2SO_4, H_3PO_4, acetic acid and citric acid and also of mixtures like KCl and HCl, KCl and KOH, K_2HPO_4 and KOH on colloidal clay. His results show that at the precipitating concentration of the different acids the $H^\cdot$ ion concentration are in the order:—

Citric > phosphoric > acetic > sulphuric, hydrochloric.

Consequently coagulation of the clay is effected by the largest quantities of $H^\cdot$ ions in the case of citric acid, then comes in order phosphoric acid. The results conclusively prove that citrate and phosphate ions are appreciably adsorbed by colloidal clay in its coagulation. Moreover, much larger quantities of dipotassium hydrogen phosphate are necessary than potassium chloride to coagulate the clay at the same $H^\cdot$ ion concentration, proving that HPO_4'' ions are more adsorbed than Cl' ions. These results are in agreement with the observation of Briggs[3] that a positively charged surface of aluminium hydroxide becomes negative in presence of citric acid due to the preferential adsorption of citrate ions.

Very recently Weir[4] has investigated the coagulation of prussian blue sol with hydrochloric, sulphuric, acetic, citric and oxalic acids, and pH values after coagulation have also been determined. From Weir's results we conclude that the order of the anions are as follows:—

$C_2O_4'' > SO_4'' > Cl' >$ citrate > acetate.

There is no reason to expect that the order of adsorption of different anions by prussian blue will be the same as with other colloids like clay, mastic gamboge etc.

In this connection it will be interesting to discuss certain results obtained by Bender[5] on the coagulation of mastic sol with a mixture of electrolytes. The following obtained by Bender are given in Tables XI-XIV.

---

[1] Kolloid-Z., **30**, 209 (1922).

[2] J. Am. Chem. Soc., **45**, 1243 (1923).

[3] J. Phys. Chem., **21**, 198 (1917).

[4] J. Chem. Soc., **127**, 2245 (1925).

[5] Kolloid-Z., **14**, 255 (1914).

TABLE XI

Coagulation by KCl and HCl

HCl 10^{-4} mole per litre	KCl 10^{-4} mole per litre observed	calculated
0.W	1045	—
7.2	0.0	—
0.91	21.75	903.05
2.05	8.7	746.5
4.10	4.35	449.5

TABLE XII

Coagulation by $MgCl_2$ and HCl

HCl 10^{-4} mole per litre	$MgCl_2 10^{-4}$ mole observed	per litre calculated
0.0	87	—
4.5	0.0	—
0.28	45.5	80.45
0.56	22.75	76.04
1.70	4.55	54.05
2.80	2.27	32.85

TABLE XIII

Coagulation by NaCl and $Al_2(SO_4)_3$

NaCl 10^{-4} mole per litre	$Al_2(SO_4)_3 10^{-4}$ mole per litre observed	calculated
1300	0.0	—
0	0.180	—
1000	0.045	0.0415
660	0.090	0.0883

TABLE XIV

Coagulation by HCl and $Al_2(SO_4)_3$

HCl 10^{-4} mole per litre	$Al_2(SO_4)_3 10^{-4}$ mole per litre observed
0.0	0.184
0.34	0.184
0.91	0.455
1.80	0.455
3.60	0.276

It will be seen from Tables XI and XII that far smaller quantities of KCl or $MgCl_2$ are required to coagulate a sol of mastic in the presence of an acid like HCl, but the deviation from the calculated values is far more marked when the sol is coagulated by a mixture of KCl and HCl than that observed when the sol is coagulated by a mixture of $MgCl_2$ and HCl. Exactly similar results have been obtained by Bender when the same sol is coagulated with a mixture of LiCl and HCl, NaCl and HCl, $MgSO_4$ and HCl, $BaCl_2$ and HCl, $FeSO_4$ and HCl etc. In all cases the deviations are more marked when the sol is coagulated by mixtures of two monovalent ions than with mixtures of a monovalent and a bivalent ion. Table XIII shows appreciable ionic antagonism when coagulation is effected by NaCl and $Al_2(SO_4)_3$, but the ionic antagonism is more marked with mixture of HCl and $Al_2(SO_4)_3$ as shown in Table XIV. Similar high ionic antagonism is observed when the sol is coagulated with mixtures of $AuCl_3$ and HCl, and $HgCl_2$ and HCl. Slight ionic antagonism is also observed with a mixture of HCl and $Ce(NO_3)_3$. All these results of Bender are highly interesting and can be satisfactorily explained from our views already advanced in the case of the coagulation of arsenious sulphide and prussian blue sols by such mixtures as KCl and HCl, and KNO_3 and HNO_3.

It is well known that mastic is weakly acidic in water due to the partial hydrolysis of the resin into masticin resene ($C_{20}H_{32}O$) and the acid $C_{20}H_{32}O_2$, which yields a very complex anion. From our researches on adsorption we have shown that an ion of high molecular weight is generally highly adsorbed. It is, therefore, expected that the anion of the organic acid is preferentially adsorbed by the mastic sol and this adsorption renders the sol more stable. Consequently, as observed in the case of A_2S_3 and prussian blue sols, the checking of this hydrolysis by an added acid will render the sol unstable and far smaller quantities of an electrolyte will be required to coagulate a sol of mastic than the calculated amounts in presence of acids. The deviations between observed and calculated values are, however, more marked with mastic sol when coagulated with a mixture of KCl and HCl than that observed with As_2S_3 sol when coagulated with the same pair of electrolytes. The results with As_2S_3 sol as obtained by us are reproduced in Table XV.

TABLE XV

Coagulation of As_2S_3 sol with a mixture of KCl and HCl.

Concentration of the sol = 0.162 grm As_2S_3 per litre. Volume = 10 c.c. Time = 1 hour.

HCl N/2 added c.c.	KCl N/2 observed c.c.	calculated c.c.
c.c.	c.c.	c.c.
0	1.40	—
0.8	0	—
0.1	1.20	1.23
0.2	0.80	1.05
0.3	0.55	0.88
0.6	0.20	0.35

From these results it is apparent that HCl can suppress the hydrolysis of mastic to a greater extent than that of As_2S_3 and hence HCl acts as a better coagulating agent towards mastic sol than for As_2S_3 sol. Table XVI will show that it is actually so:—

TABLE XVI

Coagulation of mastic sol

Electrolyte	Precipitation value
NaCl	1.00
HCl	0.010
$BaCl_2$	0.025
1/2 $Al_2(SO_4)_3$	0.0004

From Table XV we find for arsenious sulphide sol that the coagulating power of HCl is about double of that of KCl whilst from Table XVI we observe that the coagulating power of HCl is 100 times greater than that for NaCl with mastic sol and HCl is a better coagulant for mastic sol than bivalent Ba ion.

From the foregoing considerations we find that there are two important factors in the coagulation of sols like As_2S_3, mastic, etc. In presence of hydrochloric acid, the hydrolysis of the sols is checked and they are rendered unstable. This effect is far more pronounced with mastic than with arsenious sulphide. Moreover, due to the adsorption of an ion carrying the same charge as the sol, both the sols behave abnormally when coagulated by mixtures like KCl and $BaCl_2$ and LiCl and $BaCl_2$. In other words, when small quantities of KCl, LiCl etc. are added to the sols they are stabilised towards bivalent or trivalent electrolytes as shown by our experimental results on mastic and arsenious sulphide sols. Now when the above sols are coagulated by mixtures like HCl and $BaCl_2$, HCl and $MgCl_2$ etc. appreciable ionic antagonism is observed with arsenious sulphide but this antagonism is less than that observed with KCl and $BaCl_2$ or KCl and $MgCl_2$, because in presence of hydrochloric acid, arsenious sulphide sol is rendered slightly unstable due to the checking of hydrolysis and also because the ratio of the coagulating powers of $Ba^{\cdot\cdot}$ and $H^{\cdot}$ ions towards As_2S_3 is appreciably smaller than that of $Ba^{\cdot\cdot}$ and $K^{\cdot}$.

With mastic, the presence of hydrochloric acid makes the sol far more unstable towards electrolytes due to the marked checking of hydrolysis. Moreover, the ratio of the coagulating powers of $Ba^{\cdot\cdot}$ and $Na^{\cdot}$ is about 40, whilst this ratio for $Ba^{\cdot\cdot}$ and $H^{\cdot}$ is only 0.25; because of these two factors, we actually find that far smaller quantities of divalent ions like $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$. etc. are necessary for the coagulation of this sol in presence of HCl, though appreciable ionic antagonism is observed when mastic is coagulated by such mixtures as $BaCl_2$ and KCl, $MgCl_2$ and KCl.

When mastic sol is coagulated by mixtures like NaCl and $Al_2(SO_4)_3$, NaCl and $Ce(NO_3)_3$ etc. the sol is rendered appreciably unstable due to the presence of H' obtained from the hydrolysis of salts like $Al_2(SO_4)_3$, $Ce(NO_3)_3$ etc. Hence the ionic antagonism cannot be highly developed. On the other hand, when the sol is coagulated by mixtures like HCl and $Al_2(SO_4)_3$, HCl and $AuCl_3$, HCl and $Ce(NO_3)_3$ etc. because of the presence of hydrogen ion from the acid, the hydrolysis of the sol has already been checked, consequently the comparatively few hydrogen ions obtained from the reduced hydrolysis of the salts due to the presence of HCl, cannot interfere with the hydrolysis of the sol. Hence well marked ionic antagonism should be observed with HCl and $Al_2(SO_4)_3$ as the ratio of the coagulating powers of Al and H is about 35. These conclusions are supported by the experimental results of Bender on mastic sol. In Tables XVII-XIX the experimental results with As_2S_3 and prussian blue sols obtained in this laboratory are also in support of the foregoing conclusions:—

TABLE XVII

Coagulation of As_2S_3 sol with KNO_3 and $Al(NO_3)_3$. Concentration of the sol = 0.1538 gram per litre. Volume = 10 c.c. Time = 1 hour. 4 c.c. of the sol is taken each time.

N/2 KNO_3	N/1000 observed c.c.	$Al(NO_3)_3$ calculated c.c.	Percentage difference
c.c.	c.c.	c.c.	c.c.
1.4	0	—	—
0	1.65	—	—
0.1	1.25	1.53	−18.3
0.4	1.4	1.18	+18.6
0.7	1.4	0.825	+68.4
1.0	0.9	0.45	+100

TABLE XVIII

Concentration of the sol = 0.1426 gram per litre. Coagulation by a mixture of HNO_3 and $Al(NO_3)_3$.

N/4 HNO_3	N/1000 $Al(NO_3)_3$ observed	calculated	Percentage difference
1.6	0	—	—
0	1.65	—	—
0.4	1.20	1.25	−4
0.8	1.10	0.825	+ 33.3
1.2	1.15	0.41	+180.5
1.4	0.40	0.20	+100.0

With prussian blue sol only a slight ionic antagonism is observed when it is coagulated by a mixture of KCl and $Al(NO_3)_3$ as shown in Table XIX.

TABLE XIX

Concentration of the sol = 2.88 grms prussian blue per litre. Amount of sol taken each time = 1 c.c. Volume = 10 c.c. Time = 2 hours.

N/4 KCl	N/400 $Al(NO_3)_3$ observed	calculated
1.8	0	—
0	0.9	—
0.2	0.85	0.80
0.4	0.80	0.70
0.6	0.70	0.60
0.8	0.55	0.50

Bender has obtained well-marked ionic antagonism when mastic is coagulated by a mixture of HCl and $HgCl_2$. We believe that this is due to the marked adsorption of the complex $HgCl_4''$ ion by mastic.

We have already proved in a foregoing paper that As_2S_3 sol is highly stabilised by the adsorption of OH′ ions from NaOH or from a sodium or potassium salt of a weak acid. Hence marked ionic antagonism was observed when As_2S_3 sol was coagulated by mixtures like KCl and $KHCO_3$, KCl and $NaNO_2$, KCl and CH_3COOK etc. Exactly similar well-marked ionic antagonism has been observed by Bender in the coagulation of mastic sol by such mixtures as KCN and NaCl, NaOH and NaCl.

From our experiments[1] on the coagulation of mastic sol we find that greater quantities of both KCl and $BaCl_2$ are necessary to coagulate a dilute sol than a concentrated one. Similar results have been obtained by Burton and Bishop[2] with KCl and $CaCl_2$ towards the same sol. In Tables XX-XXI the results obtained by Tartar and Gailey on the influence of concentration on the coagulation of sols of mastic and gamboge by different acids are given:—

TABLE XX

Coagulation of mastic sol

Acid	milliequivalents per litre for colloid 100%	milliequivalents per litre for colloid 75%	milliequivalents per litre for colloid 50%
HCl	3.04	2.88	2.84
CH_3COOH	350.0	200.0	300.0
H_2SO_4	3.12	2.96	2.96
$H_2C_2O_4$	6.50	4.75	6.50
H_3PO_4	5.33	5.33	5.33

---

[1] J. Phys. Chem., **29**, 435 (1925).

[2] J. Phys. Chem., **24**, 701 (1920).

TABLE XXI

Coagulation of gamboge sol

Acid	milliequivalents per litre for 100% colloid	milliequivalents per litre for 75% colloid	milliequivalents per litre for 50% colloid
HCl	4.0	3.90	3.90
CH_3COOH	550.0	600.0	750.0
H_2SO_4	3.6	3.68	3.6
$H_2C_2O_4$	9.5	9.00	9.5
H_3PO_4	7.5	7.40	7.2

From the above tables we find that both mastic and gamboge have a tendency to behave normally towards dilution when coagulated by acids. These results can be explained from the following considerations:—

We have already emphasised that substances like mastic and gamboge are appreciably hydrolysed in water, and this hydrolysis renders the sols more stable towards electrolytes. On the addition of an acid this hydrolysis will be checked and the sols will be rendered unstable. The checking of hydrolysis will be more pronounced with a dilute sol than a concentrated one, when the same amount of an acid is added. Hence it is expected that a dilute sol of mastic or of gamboge will require smaller quantities of acids like HCl, H_2SO_4 etc. In other words, when these sols are coagulated by $H^\cdot$ ions they are expected to behave normally on dilution. On the other hand, the adsorption of anions by these sols will make them stable on dilution. Consequently, when these two opposing forces are counteracting each other, change in concentration of a sol should not affect the coagulating power of an acid. Moreover, it is expected that when the checking of the hydrolysis is more pronounced than the effect of the adsorption of ions carrying the same charge as the sol, it should behave normally on dilution towards $H^\cdot$ ions.

In a previous paper we have shown that prussian blue sol behaves abnormally towards dilution when coagulated by KCl, NaCl etc. We are making further experiments with prussian blue, cupric ferrocyanide, arsenious sulphide, antimony sulphide and other easily hydrolysable sols to find out whether they behave normally when coagulated by acids.

In this connection, it will be interesting to note that Tartar and Gailey have shown that in presence of small quantities of acids like H_2SO_4, H_3PO_4, $H_2C_2O_4$ etc., far smaller quantities of the corresponding salts than the calculated amounts are necessary for coagulating sols of mastic and gamboge. These results are certainly caused by the checking of the hydrolysis of mastic and gamboge and rendering them unstable towards electrolytes in presence of hydrogen ions from the added acids.

In a recent communication Kruyt and Tendeloo[1] have shown that $H^\cdot$ ions do not play such an important role as was suggested by Loeb in the coagulation of gelatine.

---

[1] J. Phys. Chem., 29, 1303 (1925).

Summary

From the foregoing considerations it will be seen that all the existing work on the coagulation of sols in presence of varying concentrations of H'' ions can be satisfactorily explained from the following facts which are emphasised in this paper:—

(1) Adsorption of ions carrying the same charge as the sol.

(2) Hydrolysis of the sols and generation of acids, which stabilise the sols. Addition of acids renders the sols unstable by checking the hydrolysis of the sols. Alkalies make the sols stable by helping such sols to be hydrolysed to a greater extent.

(3) Hydrolysis of the coagulating electrolytes.

We are at present investigating the effect of concentration of easily hydrolysable sols on their coagulation by acids.

Chemical Laboratory,
University of Allahabad,
Allahabad, India.
December, 1925.

GRAIN SIZE AND THE QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE

BY MALCOLM C. HYLAN

Introduction

In a paper[1] entitled "Dispersity of Silver Halides in Relation to their Photographic Behavior" published by the author and Dr. F. E. E. Germann it is shown that theoretically we should expect fine-grained photographic emulsions to be faster than coarse-grained ones, altho in practice the order of sensitivity seems usually the reverse. This discrepancy between theory and fact is explained on the basis of adsorption of retarding soluble halide, the fine-grained emulsions adsorbing relatively more than the coarse-grained ones, and thus reversing the purely dimensional effect. They back up their theoretical conclusions by experimental evidence, actually preparing emulsions of large and of small grains, and comparing their speeds both before and after sensitization. The sensitization was by a process calculated to remove adsorbed retarding halide. Before sensitization they found the large-grained emulsion the faster, but after sensitization, the small-grained one the faster.

Their assumption that their sensitizing process removed the adsorbed retarding halide was based on evidence described in a previous article[2] on the "Photographic Sensitiveness of Silver Iodide". That the sensitizing process does remove adsorbed retarding halide is not to be doubted, but the increase of sensitivity of the small grains over the large ones might be due, not to their size alone, but to the fact that the sensitizer, which consists of a solution of metol, pyrogallol, hydroquinone and sodium sulfite, may itself be adsorbed relatively more by the small than by the large grains, and thus produce an unequal accelerating effect. We might say, then, that the evidence by which they support their theoretical conclusions is merely "circumstantial". That is, their results are a necessary but not sufficient condition of proof of their theory. The "direct" evidence in support of their theory could be obtained only by the comparison of speeds of emulsions of different grain size, known to be free of either adsorbed retarder or adsorbed sensitizer. Such results would depend purely upon the dimensional effects of the grains.

In their discussion Germann and Hylan showed that the "effective area" of a given amount of silver halide is greater with greater dispersity, and argued that from either the continuous wave theory of light, or from the light-dart-quantum theory, a larger portion of the light incident upon the plate would be absorbed by the silver halide in small-grained emulsions than in large-grained ones, hence the speed of emulsions should be increased with increased dispersity. In a criticism of their theoretical conclusions S. O. Rawling[3] points out that Silberstein[1], in an article on the "Quantum Theory of Photographic Exposure", has shown that the number of grains hit and affected by exposure to these light quanta is given by the equation

---

[1] J. Phys. Chem., **28**, 1924, 450-456 (1924).

[2] J. Am. Chem. Soc., **45**, 2486-2493 (1923).

[3] Brit. J. Phot., **71**, 401 (1924).

$$k = N(1 - e^{-na})$$

where k = number of grains hit, N = number of grains per unit area of plate, n = number of light quanta impinging, and a = average area of grains. Rawling goes on to show that on the basis of this equation the total "effective area" of grains hit, in emulsions containing equal amounts of silver halide, will be greater for large-grained emulsions than for small-grained ones.

Both Rawling and Silberstein proceed on the assumption that every grain hit by a light quantum is rendered developable, that its developability is unaffected by absorption of further light quanta, that the amount of silver deposited by any grain is proportional to its effective area, and therefore that the total amount of silver deposited is proportional to the total effective area of grains hit, regardless of how many or how few times they have been hit. Germann and Hylan, on the other hand, assume that the developability of a grain is proportional to the amount of light it absorbs, and that the amount of silver deposited is proportional to the total amount of light incident upon the silver halide grains.

To the author, the latter view seems the more reasonable. It is a well known law of photo-chemistry that only the light absorbed has any photochemical effect. The converse, that the photochemical effect is proportional to the light absorbed, seems reasonable. If this be true, a silver halide grain absorbing two light quanta should be twice as developable as one of the same size having absorbed but one. Perhaps even, it requires the absorption of a certain minimum number of light quanta per unit mass of silver halide in the grain to render that grain developable. There is experimental evidence in support of this last assumption.

If the view of Rawling and of Silberstein is correct, we should expect the density-exposure curve to pass thru the origin, or at least come infinitely close to it, for the absorption of a single quantum by any grain should cause some silver deposit. It is well known, however, that there is a certain finite minimum value of exposure up to which the density of the silver deposit on development is zero. This can only mean that a certain finite amount of light must be absorbed by the silver halide to render it developable. Also, in certain "ripening" processes the emulsions are exposed to a subdued light, especially in the case where an emulsion is being rendered sensitive to light of some definite color, where it is exposed to light of that color. Now if the absorption of a single quantum of light rendered a grain developable, some of these grains should absorb a quantum of light during ripening and should be developable without further exposure.

The present investigation was undertaken with a view to seeing if "direct evidence" in support of the theoretical conclusions of Germann and Hylan could not be obtained, and also to see if the behavior of emulsions free of adsorbed impurities would not furnish evidence as to which of these two views, that of Germann and Hylan, or that of Rawling and of Silberstein, was more nearly correct.

---

[1] Phil. Mag., 44, 257-273 (1922).

Experimental

Equimolar quantities of potassium iodide and of silver nitrate were accurately weighed on an analytical balance, and emulsions of silver iodide prepared as follows:

EMULSION I

Solution A

potassium iodide	2.767	gms
gelatin	0.5	gms
water	15	cc

Solution B

silver nitrate	2.830	gms
water	15	cc

Warmed A to dissolve the gelatin, added B with stirring and added the mixture to a solution of 40 gms of gelatin in 220 cc of water.

EMULSION II

potassium iodide	2.767	gms
gelatin	40	gms
water	25	cc

Warmed to dissolve the gelatin then added
silver nitrate (crystals) 2.830 gms

Slides of these emulsions were prepared and examined under the microscope. Emulsion I was found to have the larger grains, being on the average 50% to 100% larger in diameter than those in Emulsion II. This result is the reverse of that obtained by Germann and Hylan in their work, and the discrepancy will be explained in the discussion.

Cards were painted with these emulsions, and after drying, were exposed and developed. Emulsion II was the faster.

Fifty cc from each of Emulsions I and II were decanted into clean beakers and 5 gms of gelatin added to each, and these modified emulsions labelled I-G and II-G respectively. Cards painted with these, exposed and developed showed them faster than I and II but II-G faster than I-G.

Forty eight cc of 20% ammonia was added to each of Emulsions I and II, and 12 cc to each of Emulsions I-G and II-G, and the resulting emulsions labelled I-A, II-A, I-G-A, and II-G-A respectively. Cards painted with these showed them to be faster than I, II, I-G, and II-G, but II-A faster than I-A, and II-G-A faster than I-G-A.

In order to approximate as closely as possible the conditions in an emulsion as usually prepared with an excess of soluble halide, cards from these emulsions were soaked five minutes in a 1% solution of potassium iodide. After drying, exposing, and developing, Emulsions I and I-G were now the faster.

Discussion

In every case, the emulsions free of adsorbed impurities showed the fine-grained emulsion faster than the coarse-grained one. On soaking in 1% potassium iodide the order of sensitivity was reversed, as was to be expected, for the fine-grained emulsion should adsorb more retarder and be slowed down more than the coarse-grained one.

These results offer direct evidence in favor of the theory of Germann and Hylan, and against the theory of Rawling and of Silberstein.

Germann and Hylan in their work found that the emulsion prepared by adding silver nitrate crystals to a solution of potassium iodide gave them much larger crystals of silver iodide than by mixing solutions of the two salts, while the author found in this investigation the reverse to be true. The key to the difference in the two cases is found in the ratio between the speed of reaction between potassium iodide and silver nitrate, and the speed of solution of silver nitrate. Germann and Hylan used large crystals of silver nitrate, some being as much as one centimeter in diameter and a millimeter thick. In this case the speed of reaction was greater than the speed of solution, leaving consequently, always a very low concentration of silver nitrate in solution. The author this time used finely ground silver nitrate in order to facilitate accurate weighing on the analytical balance. In this case the speed of solution was much greater, probably producing in the neighborhood of the crystals a fairly high concentration of silver nitrate in solution, with a corresponding decrease in size of silver iodide grains.

Summary

1. The experimental evidence offered by Germann and Hylan in support of their theoretical conclusions as to the relation between grain size and sensitivity in photographic emulsions might be regarded as merely "circumstantial".

2. Direct evidence in support of their conclusions can be obtained only by a comparison of emulsions known to be free of all adsorbed "impurities", either retarding or accelerating.

3. The quantum theory of photographic exposure as expounded by Silberstein, combined with the assumption that a silver halide grain is rendered developable by the absorption of a single light quantum, was shown by Rawling to lead to conclusions directly opposed to those of Germann and Hylan.

4. The theory of Germann and Hylan is shown to be more in accord with known facts and principles of photo-chemistry than is that of Rawling and of Silberstein.

5. Emulsions free of adsorbed "impurities" have been prepared and their speeds compared, with results which support the theoretical conclusions of Germann and Hylan.

Hale Physical Laboratory,
University of Colorado,
Boulder, Colorado.

IONIC ACTIVITY VS. CONCENTRATION IN THE INTERPRETATION OF EQUILIBRIA BETWEEN AMALGAMS AND AQUEOUS SODIUM AND POTASSIUM HALIDE MIXTURES

BY GEORGE McPHAIL SMITH

In a recent examination by Bjerrum and Ebert[1] of a series of investigations carried out during a number of years by the writer and his students,[2] the former advocate the use of ionic activities rather than concentrations, for the interpretation of equilibrium data. This affords the writer an occasion for the presentation of his own views on this subject. To him it has long seemed that so-called activities have too often been made use of merely as quantities with which to force constant values from tentative equilibrium expressions; that while the conception of activity might perhaps be a very useful one in connection with the application of thermodynamics to certain chemical processes, its usefulness would seem often to be very questionable in connection with the interpretation of chemical reactions from the kinetic molecular point of view.

It is the object of Bjerrum and Ebert to show that the data contained in the papers cited are in harmony with a recent hypothesis of the complete ionization of the strong electrolytes. They present their examination under the headings: "Transference Numbers and Conductivity," "Amalgam Equilibria," and "Some Other Properties of Mixed Salt Solutions"; but the last they dispose of in the space of less than a page. The present paper will be limited to a consideration of Bjerrum and Ebert's interpretation of the data on amalgam equilibria.

With the discussion confined to data obtained by Wells and Smith in experiments with sodium and potassium alone, and numbered into sections in order to facilitate the critical examination that is to follow, Bjerrum and Ebert's argument is as follows.[3]

A. Bjerrum and Ebert's Argument

1. "In a series of papers Smith with various co-workers has carried out a number of excellent experimental investigations of the heterogeneous equilibria between amalgams containing two light metals (Na, K) and aqueous solutions of salts of these metals.

---

[1] On Some Recent Investigations concerning Mixtures of Strong Electrolytes (Transference Numbers and Amalgam Equilibria): Kgl. Danske Videnskab. Selskab, Math.-fys. Medd., **6**, No. 9, pp. 3-20 (1925).

[2] G. McP. Smith: J. Am. Chem. Soc., **35**, 39 (1913); Smith and Ball: **39**, 179 (1917); Smith and Braley: **39**, 1545 (1917); **40**, 197 (1918); Smith and Rees: **40**, 1802 (1918); Stearn and Smith: **42**, 18 (1920); Smith, Stearn and Schneider: **42**, 32 (1920); Wells and Smith: **42**, 185 (1920); Braley and Hall: **42**, 770 (1920); Stearn: **44**, 670 (1922); Schneider and Braley: **45**, 1121 (1923).

[3] The numbering of tables and equations corresponds to that employed in Bjerrum and Ebert's paper.

"The results of these experiments are conveniently expressed in tables containing the values of the following equilibrium constant:

$$K = \frac{[K_{Hg}]\,[NaX]}{[Na_{Hg}]\cdot[KX]} \qquad (10)$$

where $[K_{Hg}]$, $[Na_{Hg}]$ denote molal concentrations in the amalgams and $[KX]$, $[NaX]$ molal salt concentrations in the aqueous phase.

2. "From the many experiments made by Smith and his co-workers we are able to see how K varies with the amalgam concentration, with the ratio between the salt concentrations, and with the total salt concentration.

"The variations of K caused by changes in the amalgam concentration do not here concern us. The values for K given in Table VI correspond to very nearly the same amalgam concentration. The salt-concentration ratio alters K to no great extent. The values for K given in the table always correspond to solutions in which the two metal salts possess the same normality.

"From Table VI it may be seen how K changes with the total salt concentration for the different salt pairs. These changes in K Smith ascribes to the existence of complexes in the salt solutions.

TABLE VI[1]

The Equilibrium Constant K at 25°

K and Na possess the same normality inthe solution.

0.15-0.20 Milliequiv. of metals per 10 g. Hg.

Ion Normality	NaCl-KCl	NaCl-KBr	NaCl-KI	NaBr-KBr	NaBr-KI	NaI-KI
0.1	0.453	0.461	0.457	0.456	——	——
0.2	0.454	0.453	0.452	0.449	0.448	0.448
0.5	0.439	0.445	0.430	0.437	0.433	0.430
1.0	0.427	0.425	0.409	0.412	0.406	0.398
2.0	0.402	0.395	0.365	0.367	0.360	0.350
4.0	0.342	0.330	0.295	0.299	0.276	0.262

3. "In the following we shall show how the changes in the K values can be explained by the hypothesis of the complete ionization of the strong electrolytes without assuming the existence of complexes.

"The lack of constancy in K is due to the use of concentration instead of activity. In applying activity in the mass-action expression we get a true constant, designated K_o.

"We have $$K_o = K.\ F_{Na}/F_K. \qquad (13)$$

Here F_s denotes the apparent activity coefficient for the ion S, *i. e.*, the ratio between the activity of the non-aqueous ion (a_s) and the concentration in the solution (c_s): $$F_s = a_s/c_s. \qquad (16)$$

4. "If we suppose complete dissociation we can assume that the deviation of the activity coefficient from 1 is due partly to the electric forces between

---

[1] Wells and Smith: Loc. cit., Cf. Tables V-X, incl.

the electric charges of the ions and partly to the hydration of the ions. Then the following relation will hold good:

$$F_s = f_s\left(\frac{p_o}{p}\right)^{m_s}. \qquad (17)$$

Here f_s denotes the decrease in the activity of the ion S, due to the electric forces, m_s the hydration number of the same ion, p_o the vapor pressure of water and p the vapor pressure of the solution.

"By introducing in (13) expressions from formula (17) and by logarithmic transformation we obtain:

$$\log K_o/K = \log f_{Na} - \log f_K + (m_{Na} - m_K) \log (p_o/p). \qquad (18)$$

5. "In order to explain the experimental data of Table VI by means of (18), we may put $f_{Na} = f_K$, since the electric forces show approximately the same effect on the activity of ions of the same valency. For K_o we may put the value to which K approaches with decreasing salt concentration ($\log K_o = -0.34$) and for log (p_o/p) the value from

$$\log (p_o/p) = 0.00421.t = 0.00421\ (3.4.c_{ion}) = 0.0143.c_{ion}. \qquad (21)$$

Here t denotes the lowering of the freezing point of the solution, c_{ion} is the salt normality of the solution, and 3.4 is a value for the molecular lowering of the freezing point which can be employed with sufficient accuracy both for the sodium and potassium salts within the range of concentrations here employed. We thus obtain:

$$\log (K_o/K) = (m_{Na} - m_K)\ 0.0143\ c_{ion}. \qquad (22)$$

"In Table VIII are given the values of $m_{Na} - m_K$, *i. e.*, the difference in the sodium- and potassium-ion hydration, obtained from equation (22), for the salt pairs: KCl-NaCl and KI-NaI.

Table VIII

	NaCl-KCl			NaI-KI		
Salt Normality	$-\log K$	$\log (K_o/K)$	m_{Na}-m_K	$-\log K$	$\log (K_o/K)$	$m_{Na} - m_K$
0.1	0.344	0.004	—	——	——	—
0.2	0.343	0.003	—	0.349	0.009	—
0.5	0.357	0.017	2.4	0.366	0.026	3.5
1.0	0.370	0.030	2.1	0.400	0.060	4.2
2.0	0.396	0.056	2.0	0.450	0.110	3.8
4.0	0.466	0.126	2.2	0.582	0.242	4.2
	$\log K_o = -0.34$			$\log K_o = -0.34$		

"For each salt pair the hydration-numbers found are sufficiently constant, but whilst the experiments with the chloride pair can be explained by the fact that sodium-ion combines with 2.2 more than potassium-ion, the experiments demand a difference of 3.9 in the hydration of the ions in the case of the iodide pair. For the other salt pairs in Table VI the changes in log K correspond to hydration differences varying between 2.2 and 3.9. Since, according to our hypothesis the hydration difference should have been the same in all cases, the variation in the hydration numbers found for the various salt pairs shows that the change of K with salt concentration cannot be ascribed exclusively to hydration. In order to explain the results of the experiments, we must assume that the various anions have specific effects on the activity of the sodium and potassium ions.

6. "From investigations on non-electrolytes we know something about the effect of such forces and hence may draw certain conclusions as to their effect on electrolytes.

"Solubility experiments with non-electrolytes have shown that the activity of these substances in solution is affected by the presence of foreign substances, both ions and non-electrolytes. These effects which have been called the salting-out effects ordinarily vary linearly with the concentration of the foreign substances. They may be explained partly by the hydration and partly by the dipole and quadrupole forces between the molecules.

"Whilst the hydration effect only depends on the depressing effect of the foreign substances on the vapor pressure of the solvent (hence mainly on the number of their molecules), the effect of the dipole and quadrupole forces is specific for the different foreign substances.

"When dealing with the activity of the ions we may, besides the effects of the hydration of the ion and of its gross charge, also expect to find effects from possible dipole or quadrupole forces. From the experience gained from the salting out of non-electrolytes we may expect that these effects will be proportional to the concentration of the reacting substance. For any definite salt pair these effects will then be proportional to the concentration, like the hydration effect. If then, as above, the hydration numbers are calculated without taking into account the effect of these forces, we get constant hydration numbers for each salt pair, but on account of the specificness of the forces, the hydration numbers calculated for the various salt pairs may differ. In order to explain the experimental results of Smith and his co-workers we must assume that the dipole and quadrupole forces between halogen-ion and alkali metal-ion vary in such a degree with the nature of the halogen that activity differences corresponding to a hydration of one or two molecules of water may appear. This is what might be expected from experiments on the salting out of non-electrolytes.

"To complete the discussion we may add that the typical ion forces, *i. e.*, the forces between the gross charge of the ions, may also lead to specific activity differences between the ions when we take into account the non-negligible dimensions of the ions."

7. According to Bjerrum and Ebert, in their summary, it has thus been shown "how the careful experiments of Smith and his co-workers, on equilibria between amalgams and aqueous solutions of salt mixtures, might likewise be interpreted without the necessity of assuming complex formation when taking into account the more recent views on the nature of electrolytes."

B. Critical Examination of Bjerrum and Ebert's Argument

The following critical discussion of Bjerrum and Ebert's study of the data obtained by the writer and his co-workers, on equilibria between amalgams and mixed sodium and potassium salt solutions, will, it is believed, suffice to show that Bjerrum and Ebert have not been fortunate in their attempt to interpret the experimental data.

1. The expression $\frac{[K_{Hg}]\,[NaX]}{[Na_{Hg}]\,[KX]} = K$ is not, as Bjerrum and Ebert designate it, an equilibrium constant; although in the case of the equivalently mixed salt pair NaCl-KCl, for example, its value should no doubt remain very nearly constant with increasing total salt concentration, if the salts really were completely ionized into simple and hydrated ions, as Bjerrum and Ebert suppose, and if in reality the excess hydration of sodium-ion over the hydration of potassium-ion remained constant, in accordance with their calculations. In the case of a specific salt pair, they have in no way accounted for a change in value of the ratio between the activities of the two cations with increasing salt concentration, so that it is hard to see how they can consider themselves to have explained the steady decrease in the value of K with increasing salt concentration.

Wells and Smith,[1] on the other hand, developed the formula $(K_{Hg})(Na^+)/(Na_{Hg})(K^+) = k$, in which (Me_{Hg}) are mol-fractions and (Me^+) are ion-fractions, as a theoretical equilibrium constant for the system, and pointed out that, since in any individual case $(NaX)/(KX) = n(Na^+)/(K^+)$, therefore $(K_{Hg})(NaX)/(Na_{Hg})(KX) = n \cdot k = C_c$,—*i. e.*, that $C_c = n \cdot k$ under specific experimental conditions, and that if C_c is found to vary with the conditions, so must n also vary. C_c was referred to in this paper as an "equilibrium expression"; since it (or B. and E's. K) varies in value with the changing total salt concentration, under otherwise identical conditions, reference to it as an equilibrium constant cannot be justified.[2]

2. The first column in Table VI, headed "ion concentration" by Bjerrum and Ebert, should be headed "total salt concentration", since the table is an assemblage of experimental data; its contents should be confined to experimental facts and not involve any theoretical views whatsoever. Neither should the table itself be headed "The Equilibrium Constant K at 25°"; the K values in the table are not constant for the different salt concentrations.

3. In the opinion of the writer, activities are too often made use of as quantities with which to force tentative equilibrium expressions to give constant values, regardless of whether anything is to be gained thereby or not.

Bjerrum and Ebert, for example, state that the lack of constancy in the K values is due to the use of concentration instead of activity, and that the application of activity in the mass-law expression yields a true constant, K_0[1]:

---

[1] Loc. cit., p. 185 f.

[2] In numerical value, our C_c is identical with B. and E's. K in the case of equilibria involving only univalent metals.

$$K_0 = K\ F_{Na}/F_K;$$

Cf. our expression $n{\cdot}k = C_0$ (or, in their terms, $n{\cdot}K_0 = K$).

They are more concerned at this point than we were with the nature of the variable n; not satisfied with n in its simple, non-committal form, they substitute for it the ratio of two unknown activities, F_K/F_{Na}, which they then proceed to analyze further into $\frac{a_K/c_K}{a_{Na}/c_{Na}}$, etc. Even if correct they would still have nothing but a more complex expression for n itself. They do later, under 5, have to assume a value for K_0, just as we had to assume a tentative value for our k.

4. Next, they assume complete dissociation and ascribe the deviation of the activity coefficient from 1 partly to the electric forces between the electric charges of the ions and partly to the hydration of the ions. On the other hand, but without any idea of complete ionization, we ascribed the deviation of n from unity in value to the existence in the solutions of hydrated or *other* complex ions, or both (see under 6).

We are therefore agreed, concerning the possible existence and influence of hydrates.

5. Finally, they attempt to explain the data of Table VI on the basis of complete ionization and some other very questionable assumptions. For example, they set $f_{Na} = f_K$, the validity of which they themselves later seem to question in their concluding remarks, under 6; and they assume 3.4 as a value for the molecular lowering of the freezing point which can be employed with sufficient accuracy both for the sodium and potassium salts within the range of concentrations employed (*namely,* 0.1-4.0 *total normality.*) Thus they develop a formula for obtaining the excess hydration of sodium-ion over the hydration of potassium-ion for the various salt pairs.

The excess hydration values calculated for sodium-ion, while probably without any significance in fact, as Bjerrum and Ebert themselves tacitly admit later under 6, are fairly constant for different concentrations in the case of a given salt pair, but they differ from one salt pair to another. Therefore Bjerrum and Ebert conclude that in addition to the hydration differences between the cations, the various anions must also have specific effects upon the activities of the sodium and potassium ions.

Since Bjerrum and Ebert assume complete ionization, since they also assume $f_{Na} = f_K$, and since in the case of a given salt pair their calculated excess hydration values for sodium-ion are the same at all concentrations, it is hard to understand the basis of their claim that they have accounted for the steady decrease in value of K, in the case of a given salt pair, with the increasing total salt concentration. Complete ionization, together with equal changes in the activities of the cations ($f_{Na} = f_K$; see 4, under A), and a constant difference in the hydration of the cations, would rather point to a more nearly constant activity ratio of the cations in the case of a given sodium and potassium halide pair, and therefore to a more nearly constant value of K.

---

[1] How could anybody apply the individual cation activities, though, without actually knowing their values?

6. A very indefinite, hypothetical discussion of the specific effects of the anions upon the activities of the cations follows, in which, in their statement that certain effects on the cations vary linearly with the concentration of the foreign substances (in this case, the anions), Bjerrum and Ebert seem to have overlooked the fact that the anions increase in concentration, as well as the cations, with increasing total salt concentration. The impression produced upon the writer at this point is that of "anything rather than admit the existence of complexes (other than hydrates) in the solutions,"—an admission, of course, which would at once concede the inadequacy of the hypothesis of complete ionization.[1]

7. At this point it will perhaps not be out of place to give a short résumé of our own interpretation of the data which Bjerrum and Ebert have assembled in their Table VI.

Smith and Wells,[2] for example, have pointed out that if, in the expression $\frac{(K_{Hg})\ (Na^+)}{(Na_{Hg})\ (K^+)} = k$, the value of k were known, the ion fractions of the metals in the individual mixtures might then be calculated by means of the formulas,

$$(K^+) = \frac{(K_{Hg})}{(K_{Hg}) + k\ (Na_{Hg})} \text{ and } (Na^+) = 1 - (K^+);$$

and that, although we are unable to ascertain the actual value of k, if we assume for k a value equal to that of C_c (or K) at $0.2N$ concentration, we can then with the use of this tentative value at least determine the direction and relative degree of the ion-fraction changes which accompany salt-concentration changes in the aqueous phase.[3]

This was done, and it was found that the K^+-ion fraction decreases while the Na^+-ion fraction correspondingly increases, with increasing total salt concentration; and that these changes take place the more rapidly, the higher the average atomic weight of the halogens in the salt pair. These results are shown in Table XII, which is here reproduced.

---

[1] Bjerrum and Ebert in their discussion have disregarded certain solubility determinations which were made in this connection by Smith and Ball (*Loc. cit.*, p. 217 f.), who, in a discussion of the effects of concentration changes upon the value of C_c (or K) in the case of equivalent mixtures of sodium and potassium sulfates, pointed out that the experimental data seemed to indicate the existence in such solutions of equilibria of the following nature,

$$Na_2SO_4 + K_2SO_4 = 2NaKSO_4 = 2\ (Me')^+ + 2\ (Me''SO_4)^-,$$

in which the intermediate ion KSO_4^-, being more stable, exists at a higher concentration than the intermediate ion $NaSO_4^-$; and that upon this basis K_2SO_4 should be more soluble in Na_2SO_4 solutions than in pure water, and that its solubility should increase with increasing concentration of the Na_2SO_4 solution. Upon investigation, this predicted behavior was definitely observed.

[2] Loc. cit., pp. 185-7.

[3] If there were any advantage to be gained by so doing, we might even claim this as a means of determining the changes in the "activity ratio" of the cations with increasing total salt concentration in solutions of the various salt pairs.

TABLE XII[1]

Ion Fraction Changes which accompany Salt-Concentration Changes in Equivalent Aqueous Mixtures of Sodium and Potassium Chlorides, Bromides and Iodides, at 25°.

		Total Normal Concentration of Equivalent Salt Mixture					
		0.1000	0.2000	0.5000	1.000	2.000	4.000
Potassium-ion Fractions Calculated at 0.2 milliequivs. of metals per 10 g. Hg, upon the assumption that *n* is here equal to unity.	NaCl-KCl	0.499	0.500	0.493	0.485	0.470	0.430
	NaCl-KBr	0.504	0.500	0.495	0.484	0.466	0.421
	NaCl-KI	0.503	0.500	0.487	0.475	0.447	0.395
	NaBr-KBr	0.504	0.500	0.493	0.479	0.450	0.400
	NaBr-KI	——	0.500	0.491	0.474	0.445	0.381
	NaI-KI	——	0.500	0.490	0.470	0.439	0.370

These ion-fraction changes we have ascribed in our paper to the existence of hydrated, intermediate and or other complex ions. We did this deliberately, on the basis of the known existence of such ions; for example, we may cite the analogous silver complexes, $[Ag(OH_2)_2]^+$, $[Ag(NH_3)_2]^+$, $[AgCl_2]^-$, $[Ag(CN)_2]^-$.

It is of course a well known fact that compounds such as $K_2[PtCl_6]$, $Na[AuCl_4]\cdot nH_2O$, $KMgCl_3\cdot 6\,H_2O$, etc. may readily be obtained from aqueous solutions; and even the alkali halides are capable of forming addition compounds with one another, as well as with other substances,[2] and these may ionize to give complex ions, especially in concentrated solutions. Certain alkali halides also show a tendency to polymerize,[3] and in recent years evidence (based upon absorption-spectra data) has been adduced to indicate that the alkali metals, through the agency of residual valency, are capable of effecting closed-ring structures, with the formation of inner-complex salts.[4] Through conductance studies of the alkali salts of certain organic acids, Lifschitz[5] has arrived at a similar conclusion.

Evidently, then, since we may have the possibility of hydrated ions and molecules, addition and polymerized compounds, and many complexes capable of furnishing ions of various species, speculation as to just what specific complex do exist in these solutions,[1] and how they behave, is more or less futile. Nevertheless, owing to the greater tendency of potassium than of sodium, and of iodine than bromine or chlorine to form complexes, we should not be surprised to find, as we do in the equivalent aqueous salt mixtures under discussion, that the potassium-ion fraction decreases with increasing total salt concentration, and the more rapidly the higher the average atomic weight of the halogens is in the mixture. And, as a matter of fact, in the case of changes in concentration, and of changes from one salt pair to another, does not this interpretation account in a most satisfactory manner for the variations in value of the so-called cation "activity ratio" of Bjerrum and Ebert? When an ion loses in concentration, as compared with another ion in the same solution, it naturally must lose in "activity" also.

---

[1] Wells and Smith: loc. cit. p. 203.

[2] Joannis: Compt. rend., **112**, 338 (1891); Abegg and Riesenfeld: Z. physik. Chem., **40**, 84 (1902).

[3] Zannovich-Tessarin: Z. physik. Chem., **19**, 251 (1896); Andrews and Ende: **17**, 136 (1895); E. W. Washburn: Trans. Am. Electrochem. Soc., **21**, 137 (1912).

[4] Hantzsch: Ber., **43**, 3049 (1910); Hantzsch and Voigt: **45**, 85 (1912).

[5] Z. physik. Chem., **87**, 567 (1914).

In conclusion, we may again be permitted to point out that ionization is too often discussed as if it were a simple dissociation alone, and that perhaps too much faith is placed in the supposition that the mass-law (a law which applies even in atomic disintegrations) is non-applicable to the dissociation of strong electrolytes; that perhaps the mass-law is less at fault than we ourselves, in our inability to determine just what molecular species are present in such solutions, and their individual chemical properties and concentrations.

At appreciable concentrations, especially in the case of mixtures, it would seem that the possible existence of complexes in solutions of (strong) electrolytes could not, without a flagrant disregard of known facts,[2] be set aside in favor of any theory whatsoever,—not even with the help of activities.

Seattle, Washington,
March, 1926.

---

[1] We may however assume, as a simple case, the following:

$$\mathrm{NaCl + KCl = NaKCl_2} \begin{array}{ll} \rightleftharpoons \mathrm{Na^+ + [Cl \cdot KCl]^-} & \quad (a) \\ \rightleftharpoons \mathrm{[NaCl \cdot K]^+ + Cl^-} & \quad (b) \end{array}$$

These addition compounds might ionize, as indicated, in either or both of two ways: (*a*) into metallic cations and complex anions, and (*b*) into chloride anions and complex cations; the complex ions may be regarded as alkali-metal or chloride ions, as the case may be, which carry alkali halide instead of (or in addition to) water. Both types of complexes are known to exist: *e.g.*, (*a*) $K_2[PtCl_6]$ and (*b*) $[(CsCl_2)_2\,Cr(OH_2)_4]Cl_3$. Concerning (*b*), see A. Werner: Ber., **34**, 1602 (1901); "Neuere Anschauungen," pp. 226, 208 (1913).

[2] For an interesting example of complex formation in the case of aqueous nitric acid, see Hantzsch: Ber., **58 B**, 941 (1924).

NEW BOOKS

A Survey of Physics. *By Max Planck. Translated by R. Jones and D. H. Williams. 19×14 cm; pp. vii + 184. New York: E. P. Dutton and Company. Price: $2.40.* This is a collection of lectures and essays arranged in chronological order but without the dates being given. The titles of the lectures are: the unity of the physical universe; the place of modern physics in the mechanical view of nature; new paths of physical knowledge; dynamical laws and statistical laws; the principle of least action; the relation between physical theories; the nature of light; the origin and development of the quantum theory.

This is a wonderfully good book. One should read it as a whole; but one can dip into it almost anywhere and be certain of finding interesting paragraphs which can be read by themselves provided one can stop then.

"What modern physicist thinks of rubbed amber when considering electricity, or, when dealing with magnetism, thinks of the small Asiatic town where the first natural magnet was found? Further, the sense-perceptions have been definitely eliminated from physical acoustics, optics, and heat. The physical definitions of sound, colour, and temperature are to-day in no way associated with the immediate perceptions of the respective senses, but sound and colour are defined respectively by the frequency and wave-length of oscillations, and temperature is measured theoretically on an absolute temperature scale corresponding to the second law of thermo-dynamics, or, in the kinetic theory of gases, as the kinetic energy of molecular motion. In practice it is measured by the variation in volume of a thermometric substance, or by the deflection of a bolometer or thermocouple. It is in no way described as a feeling of warmth," p. 5.

"While the principle of energy stands before us as a complete self-contained picture, freed from and independent of the vicissitudes of its development, this is by no means the case, to the same extent, with that principle introduced into physics by R. Clausius as the Second Law of Thermo-dynamics. Indeed, the fact that this theorem has not yet been completely established gives it a particular interest in present-day discussions. The second law of thermo-dynamics still retains a particularly anthropomorphous character in current criticism. There are several distinguished physicists who connect the question of its validity with the inability of men to penetrate the molecule and make it similar to Maxwell's demon, which, without doing work, can separate the more rapid from the slower molecules of a gas merely by well-timed movements backwards or forwards on a small path. One need not be a prophet to be able to predict with certainty that the kernel of the second theorem has nothing to do with human ability, and that its final presentation must and will follow in a manner which bears no relation to the feasibility of performing any natural processes through human agency," p. 10.

"To complete the emancipation of the conception of entropy from human experimental methods, and thereby create a real principle of the second law, was the life-work of Ludwig Boltzmann. Briefly it consists in making the conception of entropy depend upon that of probability. Thus the meaning of the word I used above is explained, namely, the *predilection* of Nature for a certain state. Nature prefers more probable to less probable states, in that all natural processes tend to the formation of states of greater probability. Heat flows from a body of high temperature to a body of lower temperature, because the state of equal temperature is more probable than a state of unequal distribution of temperature.

"The calculation of a certain measure of probability for every state of a system of bodies has been rendered possible by the introduction of the atomic theory, and of statistical methods. To determine the mutual action of individual atoms the known laws of dynamics, mechanics, and electro-dynamics can be used unaltered.

"In view of these considerations the second law of thermo-dynamics is ousted immediately from its isolated position, the mystery of Nature's predilection vanishes, and the entropy principle, bound up with the introduction of the atom into physics, becomes a well-established theorem in probability," p. 23.

"For the laws of heat radiation in free space, it must be pointed out that the constants involved, analogous to the gravitation constant, are of a universal character, since they are independent of any special substance, or any special body. Thus they can be used to determine units of length, time, mass, and temperature, and these units must necessarily retain their meaning for all time and for all extra-terrestrial and superhuman *kulturs*. It is known that this does not, by any means, hold for our ordinary weight units. Though these are usually described as absolute units, it must be borne in mind that they bear special relation to our present terrestrial life. The centimetre is derived from the present circumference of our planet, the second from its time of rotation, the gramme from water as the principal constituent of the earth's surface, and temperature from the characteristic points of water. The former constants, however, are such that the inhabitants of Mars, and indeed all intelligent beings in our universe, must encounter at some time—if they have not already done so," p. 28.

"I do not think any serious objection will be raised in physical circles when I remark that the assumption of the complete validity of the simple Maxwell-Hertz differential equations excludes any possibility of explaining, on mechanical lines, electro-dynamic phenomena in the ether. This is not altered by the fact that Maxwell originally derived his equations with the help of the mechanical theories. It would not be the first time that a correct result has been obtained from ideas associated not quite correctly," p. 55.

"The measure of the value of a new hypothesis in physics is not its obviousness but its utility. If the hypothesis proves successful, one becomes used to it and it gradually becomes obvious of its own accord. When the exploration ot electric-magnetic effects was yet incomplete, it was thought impossible to visualize galvanic streams, electro-motive force and magnetic lines of force without the aid of flow in liquids, hydraulic pumps, and stretched strings. Now, the majority of students of electro-technics scorn the use of these incomplete analogies and prefer to work directly with electro-magnetic conceptions which have become reliable through use. I have occasionally noticed that conversely, attempts have been made to illustrate complicated fluid motions, such as Helmholtz's vortex motion, by means of electro-magnetic analogies," p. 61.

"One must not imagine that advance is possible, even in the most exact of all natural sciences, without some view of the world, i. e. quite without some hypotheses not capable of proof. The theorem holds also in physics, that one cannot be happy without belief, at least belief in some sort of reality outside us. This undoubting belief points the way to the progressing creative power, it alone provides the necessary point of support in the aimless groping; and only it can uplift the spirit wearied by failure and urge it onwards to fresh efforts. A research worker who is not guided in his work by any hypothesis, however prudently and provisionally formed, renounces from the beginning a deep understanding of his own results. Whoever rejects the belief in the reality of the atom and the electron, or in the electro-magnetic nature of light waves, or in the identity of heat and motion, can most certainly never be convinced by a logical or empirical contradiction. But he must be careful how, from his point of view, he makes any advance in physical knowledge," p. 86.

"Among the more or less general laws, the discovery of which characterize the development of physical science during the last century, the principle of Least Action is at present certainly one which, by its form and comprehensiveness, may be said to have approached most closely to the ideal aim of theoretical inquiry. Its significance, properly understood, extends, not only to mechanical processes, but also to thermal and electro-dynamic problems. In all the branches of science to which it applies, it gives, not only an explanation of certain characteristics of phenomena at present encountered, but furnishes rules whereby their variations with time and space can be completely determined. It provides the answers to all questions relating to them, provided only that the necessary constants are known and the underlying external conditions appropriately chosen.

"This central position attained by the principle of least action is, however, not even today quite undisputed; for a long time the principle of conservation of energy has been a keen competitor. The latter governs in a similar manner the entire range of physics and certainly possesses the advantage of being more easily explained. It is, therefore, advisable to examine briefly the relative positions of these two principles.

"The principle of conservation of energy can be derived from the principle of least action and is consequently contained in it. The converse is, however, not true. Accordingly, the former is the more particular, and the latter the more general principle," p. 110.

"The characteristic of a theorem in probability is that it permits exceptions, and the determination of such exceptions forms an important problem in atomic statistical conception. The investigation of the conditions of equilibrium provides the most delicate proof of this. For while in dynamics equilibrium represents a condition of absolute invariability, statistical equilibrium is continually varying, more or less significant deviations referred to the so-called equilibrium of motion and, indeed, the magnitude of the mean deviation can be derived quantitatively and exactly from the theorems of probability. In this the statistical theory has established itself most brilliantly," p. 136.

"Now, the nature of electro-magnetic phenomena is no more intelligible than that of optical phenomena. To belittle the electro-magnetic theory of light, on the ground that it simply replaces one riddle by another, is to misunderstand the meaning of the theory. For its importance rests on the fact that it unites two branches of physics, which previously had to be treated as independent, and that, therefore, all theorems which are valid for one branch, are applicable to the other—a result which the mechanical theory of light did not, and could not, give. Before the introduction of the electro-magnetic theory, physics was divided into three separate branches—mechanics, optics, and electro-dynamics, and the unification of these is the ultimate and greatest aim of physical research. Though optics cannot be associated with mechanics, it combines completely with electro-dynamics, and thus the number of independent branches has been reduced to two—the penultimate step towards the unification of the physical world picture. When and how the last step will be made, the linking up of mechanics and electro-dynamics, cannot be said, and though many clever physicists are at present occupied with this question, the times does not yet seem ripe for the solution," p. 145.

"The emission of light always takes place abruptly, by impulses, for it is not determined by the regular oscillations of the electrons themselves but is only emitted when these electron oscillations receive a sudden change and a certain disruption in themselves; a kind of internal catastrophe, which throws the electrons out of their original paths into others more stable but associated with less energy. It is the surplus amount of energy liberated by the atom which travels out into space as a light quantum. Indeed, the most remarkable thing about this phenomenon is that the period of the emitted light and therefore its colour, does not, in general, agree with the period of oscillation of the electrons, either in their original or in their final paths. It is definitely determined by the amount of energy emitted, since the more rapid the oscillations, the greater is the light quantum. It follows that a short wavelength corresponds to a large amount of energy, considered as a light quantum. If, therefore, for example, much energy is emitted, we get ultra-violet or even Röntgen rays; if, however, but little energy is emitted, red or infra-red rays result. It is at present a complete mystery why the oscillations of light produced in this way are, with the utmost regularity, strictly monochromatic," p. 156.

"A question, from the complete answer to which we may expect far-reaching explanations, is what becomes of the energy of a light quantum after perfect emission? Does it spread out, as it progresses, in all directions, as in Huyghens's wave theory, and while covering an ever-larger amount of space, diminish without limit? Or does it travel along as in Newton's emanation theory like a projectile in one direction? In the first case the quantum could never concentrate its energy in a particular spot to enable it to liberate an electron from the atomic influences; in the second case we would have the complete triumph of Maxwell's theory, and the continuity between static and dynamic fields must be sacrificed, and with it the present complete explanation of interference phenomena, which have been investigated in all details. Both these alternatives would have very unpleasant consequences for the modern physicist," p. 178.

Wilder D. Bancroft

Colloid Symposium Monograph. *Vol. III. Edited by Harry N. Holmes. 24×17 cm; pp. 323. New York: Chemical Catalog Company, 1925. Price: $5.00.* This volume contains the papers presented at the meeting in Minnesota last June. The authors and titles are Herbert Freundlich, On the Electrokinetic Potential; W. D. Bancroft, Molecular Weight and Solution; P. Lecomte du Noüy, Some New Aspects of the Surface Tension of Colloidal Solutions which have led tc the Determination of Molecular Dimensions; Irving Langmuir, The Distribution and Orientation of Molecules; S. E. Sheppard, Photographic Sensitivity; L. H. Reyerson and Kirk Thomas, Catalysis by Metallized Silica Gel; H. T. Barnes, Colloidal Water and Ice; L. S. Palmer and G. A. Richardson, The Colloid Chemistry of Rennet Coagulation; L. V. Heilbrunn, The Colloid Chemistry of Protoplasm; W. P. Larson, H. O. Halvorson, R. D. Evans, and R. G. Green, The Effect of Surface Tension Depressants upon Bacterial Toxins; I. N. Kugelmass, Physico-chemical Studies of the Mechanism of Blood Clotting; L. B. Miller, The Effect of Anions upon the Physical, Colloidal, and Chemical Properties of Aluminum Hydroxide; P. L. Gile, Nature of the Colloidal Soil Material; Emil Truog, The Colloid Chemistry of Soils; F. J. Alway, The Power of Soils to absorb Water from Air; C. A. Mann, The Mechanism of Lithopone Formation; A. J. Stamm, An Experimental Study of Emulsification on the Basis of Distribution of Size of Particles; J. B. Nichols and H. B. Liebe, The Centrifugal Method for the Determination of Size of Particle of Suspended Material; William Seifriz, Elasticity and Some Structural Features of Soap Solutions; L. V. Foster, A Simplified Slit Ultramicroscope; W. J. Kelly, The Plasticity of Rubber and its Sols; W. G. France, A Motion Picture Study of the Influence of Gelatin on Rates of Crystal Growth and Solution of Copper Sulphate.

This is rather an impressive list of papers and they are a great deal better than they seemed to be at the Symposium where most of them were presented at much too great length. By the electrokinetic potential Freundlich means the single potential which we obtain in cataphoresis and electrical endosmosis cases. It is the potential difference between the solution and an adsorbed liquid film on the electrode and may therefore be quite different from the ordinary or thermodynamic potential. This gives a plausible explanation for the difference between the Ostwald zero and the Billitzer zero. The only difficulty with this is that one would suppose that the flowing mercury electrode should give the electrokinetic potential, whereas it actually gives the thermodynamic potential. Freundlich's experiments seem to show that adsorption plays a great part in the electrokinetic potential and only a slight part in the thermodynamic potential. This may be true but it is not clear why it should be. There is no apparent reason why one should not have marked adsorption at the surface of the metal.

Sheppard says that "it has long been known to emulsion makers that different varieties and batches of gelatin used to prepare the same emulsion could give quite different photographic qualities and notably different sensitivities." From special experiments he concluded that "the sensitivity substance is specifically afforded by the gelatin, and in greater degree by one gelatin than by another." A long and skilful study has proved that "the sensitizing body in photographic gelatin is primarily allyl isothiocyanate, which becomes partly converted to allyl thiocarbamide," which may react with the silver halide to form silver sulphide. "The sensitivity substance discussed in the first part of this paper is, therefore, silver sulphide Ag_2S, which can be replaced by Ag_2Se or Ag_2Te with equal or greater effect. This substance is consistent with the theory developed for the function of the sensitivity nuclei.

"Silver sulfide is known to be capable of acting as nucleus in silver reductions. Further, its presence in the silver halide lattice would correspond to a sphere of disorientation (and ionic deformation) of the silver halide about it. It has been pointed out by G. von Hevesy that the smaller the ratio of electrolytic conductivity just above and below the melting point, the easier the orientation of the atoms in a (heteropolar) crystal lattice. For example, with the halides, . . . this condition increases up to silver iodide. This disorientation tendency is further related to the electron affinity of the ions forming the crystal. The smaller the work necessary to convert the ions forming the crystal into the neutral state, the greater the disorientation tendency of the crystal. This principle is, moreover, reversible, and is fully in harmony with the theory of the sensitizing function proposed. . . . Silver iodide not only shows the greatest disorientation tendency, but lowest electron affinity. But further, as von Hevesy points out, sulfur has an electron affinity of only 45 kg. cals., and solid Ag_2S shows an even greater conductivity than solid AgI, being the best known electrolytic conductor."

Palmer and Richardson have controverted Alexander's theory of the clotting of cow's milk by rennin by showing that lactalbumin does not act as Alexander had assumed and that there is no warrant for Alexander's alleged assumption that the casein compound natural to cow's milk is an unstable, irreversible colloid. The reviewer does not know whether Alexander really made this assumption or not; but it is not essential to his theory. One can consider that casein is peptized by lime and yet admit that the so-called "calcium caseinate dispersion is itself a protective colloid of a high order, emulsifying fats, protecting gold sols, and exhibiting other properties of emulsoid sols." A case in point is an alkaline chromic oxide sol. The reviewer holds no brief for Alexander; but the paper would have been more satisfactory if the authors had been a little fairer in their discussion.

Heilbrunn conceives of protoplasm "as consisting of an interior mass of fluid surrounded by a precipitation membrane of the Traube type. The interior fluid is a protein sol and contains various granules and droplets suspended in it. . . . As soon as it became at all apparent that the living material was a fluid or a semi-fluid, as soon indeed as the biologists began to think of it in physical terms, they suggested that in its various activities it might suffer coagulations like those which had previously been observed in such animal fluids as blood and milk. But it is easier to demonstrate the coagulation of blood or milk than the coagulation of protoplasm. Only with the development of reliable methods for viscosity determination within the living cell has it been possible to show conclusively that at least one process is associated with a coagulative change or at any rate a change involving a great increase in viscosity. Thus it was found in 1915 that the early stages of cell division in seaurchin eggs were accompanied by a sharp increase in viscosity. This knowledge has now been confirmed for plant cells."

"Perhaps it may be worth our while to reason about the colloidal phenomena of muscle and other living structures in an indirect way. If the effects of chemicals on protoplasm are the same for various sorts of protoplasm, and we have reason to believe within fairly wide limits that they are, then we can apply our knowledge of such effects to the interpretation of biological processes, even in those instances where there are at present technical difficulties in the way of a direct determination of the protoplasmic viscosity. Thus for example if it is true, and I think it is, that a higher proportion of sodium ions in the medium surrounding a cell or group of cells tends to produce an increased viscosity and that an increase in the proportion of calcium ions tends to have the opposite effect, then if it is found that sodium ions stimulate a muscle to contraction and that calcium ions tend to prevent such a contraction, we have reason for assuming that the contraction process is in some way associated with increased viscosity of the protoplasm. Actually it has been shown for a long time that sodium ions do stimulate muscle cells to contract and that the addition of calcium ions tends to prevent this action."

Truog sums up his work on the colloid chemistry of soils by saying that "the question of soil acidity is intimately linked with the colloids of the soil. When the colloidal silicates, the acid silicates, and the alumino-silicic acids, are largely neutralized due to an ample supply of bases, the soil solution cannot become acid due to the ease with which bases are secured from these colloids. When the colloidal acids, just mentioned are less completely neutralized, bases are not secured so easily and as a result the nitric and sulfuric acids which are formed in the decomposition of organic matter may not become completely neutralized, giving rise to an acid solution. The relatively insoluble colloidal soil acids, as has been shown, have a sufficient solubility to cause an acid reaction of the soil solution."

Stamm reports a case in which "the emulsifying agent is soluble in both phases. Emulsions of amyl alcohol in water result regardless of which phase the soap is dissolved in, and from qualitative tests appear to give the same dispersity."

Wilder D. Bancroft

Die Methoden der Organischen Chemie. *Vol. II. By J. Houben (and collaborators) Third edition. 17×26 cm; pp. 1431. Leipzig: Georg Thieme, 1925. Price: paper 75 marks, cloth 84 marks.* The second volume of Houben's "Die Methoden der Organischen Chemie," 3rd Edition, is now available, and comprised within its 1431 pages is a mass of information of interest to the organic, the physical, and the technical chemist. Indeed no one carrying out practical research work, whether of a purely scientific or technical character can afford to be without this very valuable work of reference.

The bias throughout is practical, the previous tradition having been maintained. The book is a treatise on "Methods". There is an index consisting mainly of the names of substances, but even more useful is the carefully drawn up table of contents, a glance at which reveals the plan underlying the general arrangement and enables the description of any process or method to be located with facility.

The scope of the work may be gathered from the fact that the following subjects, amongst others, are treated in detail: catalysis, electro-chemical methods, reactions at high pressure, photochemical methods, oxidation, reduction, addition reactions and condensation, optical resolution and the Walden inversion, and enzyme action. Remarks on one or two of these sections may be appropriate.

The chapter on catalysis extends over 126 pages and includes detailed descriptions of the methods for preparing contact material in an active condition—nickel for the Sabatier-Senderens process, platinum black for Willstätter's method, colloidal palladium for Paal and Skita's, etc. Descriptions and diagrams are given of the special apparatus employed. Then, with the aid of many examples, some of which are described in detail, the methods and experimental conditions which have been found most suitable for bringing about various types of reactions are discussed. Considerable space is devoted to the technically important process of hydrogenation and dehydrogenation. The conditions under which high pressure, with and without high temperature, is necessary are discussed and the appropriate experimental procedures are described. Non-catalytic methods of hydrogenation and dehydrogenation are, of course, dealt with in the section on reduction and oxidation, and a more general treatment of the subject of high-pressure reactions is given in a special chapter under this title.

Similarly, the chapter on electro-chemistry deals, in the first place, with apparatus, and the methods of making the preliminary electrical measurement necessary in establishing a given set of experimental conditions. Then numerous illustrations are given of the types of conditions that have been found most suitable in certain classes of cases. It should be said that this chapter contains one or two rather conspicuous lacunae· thus no mention is made of Crum Brown and Walker's classical work on the electrolysis of the salts of carboxylic acids. The tendency manifest throughout the whole book to draw illustrations mainly from German sources, whilst it does not impair its general usefulness, seems to be responsible for some of the more obvious gaps in the subjects treated.

The section on photochemical reactions is one of the best, containing as it does not only a remarkably complete account of the action of light on organic compounds, but also a copiously illustrated description of various light sources and light filters, tables of limits of transparency, maps of spectra, and other useful data.

From the standpoint of ordinary organic chemistry it is impossible to speak too highly of the book, which, during the few weeks it has been in the reviewer's hands, has shown the exit from a difficulty on several occasions.

C. K. Ingold

Der Wasserstoff. *By Alfred Stavenhagen. No. 76 of Sammlung Vieweg. 14×21 cm; pp. 104. Braunchweig: F. Vieweg, 1925. Price: 5 marks.* The manufacture of hydrogen for industrial purposes is constantly increasing in economic importance. The stimulus given by the development of aerial navigation to work on the preparation of this gas was intensified some fifteen years ago by the application of hydrogenation to the liquid glycerides for their conversion into higher-priced solid fats. Hydrogen requirements have since grown to yet larger dimensions in connection with the synthesis of ammonia and the world's consumption for this purpose is likely to increase considerably in the near future. Any addition to our knowledge of this common element, and its isolation from its compounds or from admixture with other gases must be welcome.

The brochure under review cannot be said to add much to the store of published information or to make the available material more valuable by critical discussion. It is mainly a brief compilation of the patent and other literature without an attempt being made at assessing the various processes at any but their face value. The physical chemist will be disappointed with the scant consideration given to their fundamentals.

The methods of hydrogen manufacture dealt with are, the decomposition of water by metals or metallic hydrides, the action of acids or alkalies upon metals, the decomposition of water by carbon, the scission of hydrocarbons, the electrolysis of water. A concise summary of the chemical and physical properties of hydrogen, its physiological action, its use, storage and transport is given.

Mis-spelling of names, such as Bode and Howard, instead of Bone and Coward,—Langner instead of Langer, and the bracketing of the first-named authors to other, independent workers by a single reference (page 54) is a blemish not usually associated with the proverbial thoroughness of German authors. Some of the illustrations taken from pre-war catalogues of German manufacturers are known to those interested in the subject. A chronological list of Patents, completed by the inclusion of some notable omissions, would add to the value of the book for ready reference.

R. Lessing

Textile Chemistry. *By F. G. Cooper. 23 × 16 cm; pp. ix+235. New York: E. P. Dutton and Company. Price: $5.00.* The book is written for the classes in the Union of Lancashire Institutes and in the City and Guilds of London Institute; but "it should appeal also to the young studious cotton operative who desires to increase his technical knowledge, and to those in positions of authority in mills who wish to know something of the nature, preparation, and properties of the materials used in the various processes through which cotton must pass in its journey from fibre to marketable cloth."

There are twelve chapters on general chemistry entitled: chemical diagrams; glass manipulation; simple processes; classification of matter; water; gases; oxygen; acids, alkalies, bases, salts; the elements of chemical theory; carbon; chlorine; aluminum, etc. This is followed by six chapters on the application of chemistry to textiles: the natural fibres; the machinery; sizing; bleaching; dyeing; mercerizing.

It is very difficult to judge a book of this sort, because we give much more chemistry in the high schools than is contained in this book. It might appeal to an ambitious mill hand who had had no chemistry.

The reviewer was a little startled to read, p. 105, that one of the uses of carbon dioxide is as an indicator of impurities in an atmosphere—*e.g.* in mills and schools. While it is true that Seidlitz powders, health salts, and fruit liberate carbon dioxide when mixed with water, it seems to be a little far-fetched to say that therefore one of the uses of carbon dioxide is for medicine. The reviewer had supposed that salts were made effervescent to make the medicine more appetizing and not to make it more effective.

It was new to the reviewer that "bottles of ether should be kept on the floor and never on a laboratory bench. Very disastrous consequences have occurred due to inattention to this simple precaution," p. 119. The author adopts the view of Gladstone on the theory of mercerization and writes a formula, p. 228, for the hypothetical salt of cellulose.

Wilder D. Bancroft

FRICTIONAL ELECTRICITY

BY HERMANN F. VIEWEG

Introductory

It was known to the ancients that substances like glass or amber acquire the peculiar property of attracting small pieces of other matter when rubbed with cloth or fur. The attraction between the loadstone and iron was also known. It was not realized that these phenomena were distinct, and the earlier writers did not differentiate between them.

Gilbert[1], in his interesting treatise on the magnet, pointed out that these attractions were of two kinds. The first was that between iron and the loadstone; this he called magnetic. The other was the attraction exerted by amber on small bodies. Gilbert discovered that a number of other substances could acquire this same property of attraction, and he devised a simple electrometer to study their action. Those bodies which like amber (ἤλεκτρον) would attract others when rubbed he called "electrics"; others which lacked this property he called "an-electrics". Gilbert may thus be said to have started the study of frictional electricity.

During the seventeenth and eighteenth centuries, numerous investigations were undertaken; these, however, were directed mainly towards a study of the properties and action of the frictional electricity, developed by rubbing a few standard substances, rather than towards the examination of new substances, or an explanation of the origin of the electricity. The accounts of many of these experiments are interesting, and often very amusing, but they are of little scientific value to us at present.

For a long time, a substance was thought of as being either distinctly positive, or distinctly negative, and it was believed that the sign of its charge would normally be the same whenever it was rubbed. Wilcke[2] was the first to bring out the idea that materials could be arranged in a series grading from those with the greatest tendency to become positively charged to those becoming most readily negative. Thus any member of the series might become either positively or negatively charged, depending on the substance with which it was rubbed. Wilcke arranged a few materials in order, thus establishing the first simple frictional electric series.

Various other investigators since then have worked along the same line, adding new substances, and re-arranging those already studied. Among these should be mentioned Faraday,[3] who established a series, more complete than the previous ones. He determined the fact that water must be at the positive end of the series since it charged everything else negatively.

---

[1] Guilielmi Gilberti Colcestrensis: "De Magnete," Book II, Chapter II, London (1600).

[2] Wilcke: Phil. Trans., **11**, 401 (1759).

[3] Faraday: Exp. Res., **2**, 2075-2145 (1843).

As the subject was studied more and more, it was found that arranging such series was not quite as simple as it seemed. Thus, although Riess[1] believed that every substance had its own definite position in a frictional electric series, he had difficulties in proving it, because of certain contradictory results he encountered. He explained these as being due to abnormal surface conditions, the effect obtained not being characteristic of the material itself. In spite of these troubles, Riess managed to arrange most of the things he studied in a series. His most valuable achievement was the determination of the fact that an equal amount of both kinds of electricity is generated by friction.

While some were working to arrange various materials in order, others were more interested in developing the laws governing the generation of frictional electricity. Peclet[2] made a thorough study of a few substances, and found that there was a definite maximum surface density of charge which one substance could acquire by friction on a specified second substance. This maximum he found was independent of the velocity of rubbing, the pressure applied, and of the area of surface involved. Riecke[3] derived the mathematical expressions showing the relations between the density of charge, the area of surface, and the rate of rubbing. His calculations, as he showed, agree quite satisfactorily with the results of Riess.

With all these data of many workers available, it was to be expected that efforts would be made to offer an explanation for the cause of frictional electricity. In 1879, Helmholtz[4] proposed the theory that the fundamental cause is a contact difference of potential which exists between any two materials. According to this theory, when two unlike surfaces are brought together, there is a concentration of positive charge on one surface and of negative on the other. It can be shown theoretically that on separating the two, if either be a non-conductor, the contact potential difference is greatly magnified, and the two surfaces will therefore be charged oppositely and at very high potentials. If both surfaces are conducting, the charges will neutralize each other on separation, at the last instant that the two substances are in contact at any point. Thus two insulators, or an insulator and a conductor, will remain charged after separation; in the case of two conductors no appreciable charge persists.

This view was supported by Hoorweg,[5] who measured the contact potential differences between various materials. He found that friction between two substances charged them the same way as one would expect from their difference of potential while in contact. The existence of a contact difference of potential between metals and insulators, as well as between insulators themselves, was shown experimentally. Hoorweg believed that the charges were due in part to a thermo-electric effect caused by local heating due to friction.

---

[1] Riess: Pogg. Ann., **236**, 589 (1877).

[2] Peclet: Ann. Chim. Phys., **57**, 337 (1834).

[3] Riecke: Wied. Ann., **3**, 414 (1878).

[4] Helmholtz: Wied. Ann., **7**, 337 (1879).

[5] Hoorweg: Wied. Ann., **11**, 133 (1880).

Further study of contact difference of potential between various materials was made by Christiansen.[1]

The Helmholtz theory does not predict what the relative polarity of two substances should be. Attempts have been made to determine the relation between other physical properties and the position in a frictional electric series. After investigating quite a number of di-electrics, Coehn[2] postulated the following: The order of non-conductors is the same as that of their di-electric constants, the higher di-electric constants corresponding to a greater tendency to become positively charged. In a later investigation it[3] was also shown that the difference of potential is proportional to the difference in di-electric constant.

On the other hand, Hesehus[4] believed it was a question of the relative density of the surfaces, the more dense becoming positively charged, electrons flowing to the less dense, this being aided by a change in the surface tensions at the points of contact.

It has been shown by Melander[5] that the temperature of a substance affects radically the sign of charge that it acquires on being rubbed. The few materials investigated by him became more easily positively charged as their temperatures were increased. He proposed the idea of "electronic temperature" as distinct from the ordinary molecular temperature. Two substances at the same molecular temperature will in general have different electronic temperatures, the substance having the higher giving up its electrons more readily than the other. With an increase in heat content, the electronic temperature will also be raised, and the tendency to acquire a positive charge increased. Thus a reversal in the potential difference might be expected if the ordinarily negative substance were heated sufficiently.

Although the study of frictional electricity has not reached the point of being a quantitative science, a few researches of a quantitative nature have recently been carried out. Morris-Owen[6] has studied the relation between the frictional work done in rubbing and the magnitude of charge developed, varying the pressure exerted between the two surfaces. It was found that the maximum surface density of charge obtainable was independent of the pressure used in rubbing, but that the greater the pressure applied, the smaller was the work required to attain the maximum charge.

Similarly, Morris-Jones[7] measured quantitatively the maximum charge of several materials when rubbed with silk, flannel, and chamois leather; also of certain metals rubbed with silk. Assuming that the rate of charging was proportional to the rate of work, and that the charge leaked from a surface at a rate proportional to its charge, an expression was derived showing how the charge varied with the work done. The maximum charge would be attained when the rate of charging just equalled the rate of leakage. The results obtained agree quite well with the values predicted.

---

[1] Christiansen: Wied. Ann., **53**, 401 (1894).

[2] Coehn: Wied., **64**, 217 (1898); **66**, 1191 (1898).

[3] Coehn: Ann. Physik, (4) **30**, 777 (1909).

[4] Hesehus: Physik. Z., **2**, 750 (1901); J. Russ. Phys. Chem. Soc., **34**, 1 (1902); **35**, 575 (1903); **37**, 29 (1905).

[5] Melander: Physik. Z., **8**, 700 (1907).

[6] Morris-Owen: Phil. Mag., **17**, 457 (1909).

[7] Morris-Jones: Phil. Mag., **29**, 261 (1917).

The recent work of Shaw[1] is no doubt the most complete and thorough investigation that has yet been made of the generation of frictional electricity. A large number of substances were arranged in a "tribo-electric" series. The surfaces, in addition to being studied under normal conditions, were investigated under abnormal conditions, such as after and during heating; under great pressure; while flexed; and after polishing or grinding. The general effect of each of these abnormalities of surface was determined.

Shaw divided all his materials into two groups, "A" and "B", depending on how they acted under these abnormal conditions. He postulated that there were two oppositely charged layers near the surface of any substance; those in group "A" having the negative layer outside, while in group "B" the positive layer was outside. Abnormal conditions would cause a disarrangement of these layers and might even reverse their positions. No explanation was given to show why any particular substance should belong to the group in which its tribo-electric properties placed it.

All that has been done in this field up to the present may be summarized as follows:

Various frictional electric series have been established, and a considerable number of materials have been assigned their positions in them.

The relation between position in the series and other physical properties, especially the di-electric constant, has been pointed out.

A few quantitative researches have been undertaken.

The effects of certain abnormalities of surface have been studied.

The existence of contact differences of potential between different solids has been shown.

No satisfactory explanation of the causes and origin of frictional electric charges has been given.

A Frictional Electric Series

The present investigation was undertaken with the following objects in view: (1) to arrange a frictional electric series of suitable materials, (2) to explain, if possible, from such a series how various factors determine the position a substance takes, (3) to learn what the effect of moisture is, and to what extent this may account for anomalies previously observed.

The first step, then, was to study a group of materials, chosen as adapted to the purpose, with reference to the charges produced when different surfaces are rubbed together; and from the results to arrange a frictional electric series. In selecting the materials to be used, it seemed best to use crystalline substances of definite composition, and to observe the effect of definite faces. Many of the materials usually employed by other investigators are of such indefinite nature that it does not seem probable that results obtained with them can be interpreted; nor are they always reproducible. Such substances as furs, while they serve excellently in the generation of frictional electricity, are surely of quite variable properties. It does not seem reasonable to require all cats to have furs with identical electric characteristics. In fact, Shaw found in his experiments that one fur might vary from one part to another, being positive at one point and negative at another, with reference to the same substance. Nor is one impressed with the dielectric constant of bacon as being an accurately defined physical property. Similar objections apply to such indefinite substances as "filter-paper," "blotting-paper", "sealing-wax", "wood", et cetera. In using such things, one is merely adding unknown factors, without which the problem is already sufficiently complicated.

---

[1] Shaw: Proc. Roy. Soc., **94A**, 16 (1917).

On the other hand, we are dealing with something absolutely definite when we use a specified face of a specified crystalline substance. While, of course, not all the crystalline structures of the materials studied are known, they nevertheless do have definite structures, the properties of specific faces are definite, and results can be duplicated. In many cases, the arrangements of the component atoms have been determined, and we know just how each face is constructed. Also, sufficient work has been done on the distribution of electricity in atoms, to give a good idea of how they are made up.

The attitude adopted in this part of the investigation has been that the ultimate solution of the problem lies in a consideration of the electrical structure of the surfaces in question, and that the bases for such a consideration are, first, the arrangement of the component atoms, for which one depends chiefly on the results of X-ray analysis,[1] and, secondly, the structure and electrical properties of the atoms themselves, as indicated by the theoretical and experimental results of the Bohr and Lewis theories.[2]

In accordance with this view, various crystals were used, these being mainly well-crystallized minerals, the choice of those to be used depending to some extent on what was readily available. In addition, a few of the standard materials were used, in order to correlate this series with others previously established.

In the experimental work itself, care was exercised to avoid as much as possible all effects that might cause anomalous and inconsistent results. In particular, attention was paid to having the surfaces clean and dry. Fresh surfaces were broken where possible, as with minerals having good cleavage, others were scraped, and metals, were cleaned either chemically or mechanically. All substances were dried over sulfuric acid before testing.

The specimen to be investigated was fastened with sealing-wax or glue to a glass rod about 10 cm. long. This served as an insulator and also allowed materials to be handled at sufficient distance to prevent loss of charge by induction. The other end of the rod was equipped with a wire hook, so that it might be hung up in a desiccator.

---

[1] See W. H. and W. L. Bragg: "X-Rays and Crystal Structure" (1924).

[2] See Andrade: "The Structure of the Atom" (1924).

In rubbing two surfaces together, a pressure was applied, and the rubbing done rather vigorously. It was found that successive results might be inconsistent unless this was done. This is no doubt due to the adsorbed films which exist on some surfaces, the properties of which, rather than those of the surfaces themselves, are tested by gentle rubbing. Such films may be removed or penetrated by proper application of force.

To measure the charges so obtained, use was made of a sensitive electrometer, of the Dolezalek quadrant type. One set of quadrants was grounded, the other connected to a simple condenser at about two metres distance. This consisted of two circular copper plates of 3 cm. radius, separated by a glass plate, 3 mm. thick. The needle of the electrometer could be charged to a negative potential of 55 volts, from the negative terminal of a direct-current line. A U-tube of water was put in series with the instrument, this high resistance protecting it in case of short-circuit inside the electrometer, and still allowing the potential difference of 55 volts to be maintained. All wiring from the electrometer was thoroughly insulated, a grounded copper tube enclosing the rubber tubing in which the wiring was contained. The instrument itself was surrounded by a grounded metal container. These grounded conducting shields were a protection from outside electrostatic effects. The image of a lamp, reflected from the mirror of the electrometer, was focussed by a lens on a scale, about three metres distant.

No attempt was made at quantitative measurements, although it was desired to have some idea of the magnitude of the charges. When the upper plate was charged to a potential of 15 volts, the electrometer deflection was 20 scale divisions. The capacity of the two plate condenser can be calculated to be .00005 microfarads. A charge of 4×10^{-11} coulombs, or 2.5×10^{-8} electrons, was therefore equivalent to one unit of the scale. On this basis, the charges were found to vary between 10^{-9} and 10^{-10} coulombs, and in each case equal and opposite on the two substances.

Using the method just described, the following series was established, each substance being charged positively on rubbing with any one below it, and negatively by any above it. The composition, crystallization, and crystal face used, is stated for each member of the series, except that where no crystal face is mentioned, massive or non-crystalline specimens were used.

Discussion

Whenever two unlike surfaces are brought into contact, there is a tendency for electrons to pass from one surface to the other. As a result, that surface which possesses the greater attraction for electrons or the lesser power to emit them becomes charged negatively, while the other acquires an equal positive charge. We may think of each substance as having a characteristic electron pressure; or, as Melander calls it, an electron temperature.

That two metals have a definite contact potential difference, a function of the temperature, is well-known from the Peltier effect. In the case of two non-conductors or of a non-conductor and a conductor a contact potential

TABLE I

The Frictional Electric Series

Positive End of Series

Substance	Composition	Crystallization.	Face
Serpentine	$H_4Mg_3Si_2O_9$	Monocl.	
Asbestos	Silicate		
Fur	Organic		
Topaz	$(AlOH)_2SiO_4$	Rhombic	001
"	"	"	$00\bar{1}$
Mica	$KH_2Al_3(SiO_4)_3$	Monocl.	001
Glass	Silicate		
Calcite	$CaCO_3$	Hex.	$(1\bar{1}00)$
"	"	"	$(1\bar{1}01)$
Aragonite	"	Rhombic	(001)
Cheesecloth	Organic		
Barite	$BaSO_4$	Rhombic	(110)
"	"	"	
"	"	"	(001)
Quartz	SiO_2	Hex.	$(1\bar{1}00)$
"	"	"	$(1\bar{1}01)$ or $(\bar{1}101)$
Magnesium	Mg		
Fluorite	CaF_2	Isometric	(111)
Lead	Pb	"	
Fluorite	CaF_2	"	(100)
Gypsum	$CaSO_42H_2O$	Monocl.	010
"	"	"	$0\bar{1}0$
Celestite	$SrSO_4$	Rhombic	(001)
Zinc	Zn	Isometric	
Orthoclase	$KAlSi_3O_8$	Monocl.	(001)
Anhydrite	$CaSO_4$	Rhombic	
Beryl	$Be_3Al_2Si_6O_{18}$	Hex.	$(1\bar{1}00)$
Blotting paper	Organic		
Sealing-wax	"		
Sphalerite	ZnS	Isometric	(110)
Magnetite	Fe_3O_4	"	(111)
Galena	PbS	"	(100)
Pyrite	FeS_2	"	(210)
Molybdenite	MoS_2	Hex.	(0001)
Copper	Cu	Isometric	
Antimony	Sb	Hexagonal	
Stibnite	Sb_2S_3	Rhombic	
Silver	Ag		
Silicon	Si		
Sulfur	S	Rhombic	
Rubber	Organic		

Negative End of Series

difference has been found by Helmholtz, by Hoorweg, and by Christiansen. Melander's work indicates that this, too, varies with the temperature.

The existence of such a difference of potential is disputed by Morris-Owen, because he could obtain no frictional charge from mere contact of two dielectrics. The real reason for this is that mere touching does not bring any appreciable area of either substance into contact with the other. Even rubbing does not bring a large percentage of the total area into effective contact. This is indicated by the fact that when a crystal is pulled apart on a cleavage plane where opposite faces are unlike, the charges so developed are very much larger than those obtained by rubbing the same surfaces together. One cannot hope by rubbing the smoothest surfaces to bring a large portion of the total area into real contact. It is therefore reasonable to expect that mere touching has no great effect. On the other hand, the fact that the separation of two surfaces in actual contact at molecular distances, without any rubbing, causes such great charges, is strong evidence in favor of a contact potential difference.

Shaw has expressed the opinion that, if the charge is due to a transfer of electrons, the metals with all their "free" electrons ought to be at the positive end of the series. Since they are not, he doubts the explanation given here. There seems to be no basis for such an objection. The electrons of a metal may be "free" in the sense that they can readily move through the material when the proper potential difference is applied, but there is no excess of electrons ready to be given up, when a metal is at zero potential. Hence a metallic element will take its place in the series according to its electronic structure, and not at a special place due to its metallic nature.

Let us consider what happens when two unlike surfaces are in contact. Electrons from each substance will, in their rotations or oscillations, come within the sphere of activity of some atom of the other substance. Occasionally one of the electrons, being more strongly attracted by a positive nucleus with which it was not originally associated, will stay with it. There will be a mutual exchange of electrons; but that surface which loses electrons less readily will get more than it gives up. On separation it will have acquired a negative charge, the other a positive charge.

The direction in which the effective transfer of electrons takes place is dependent on the nature and structure of the atoms in each surface. Each atom is a definite aggregate of electricity; the atoms are arranged in a definite manner in crystalline matter, but in a random way in amorphous matter. Experimentally it is found that the nature of the atoms, that is, the chemical composition of the surface, is a more important factor than the arrangement of the atoms. This is shown by the fact that, although different faces of the same crystal have different positions in the series, the general position of a chemical compound is independent of the face used. In the case of $CaCO_3$, the two crystalline forms, calcite and aragonite, occupy adjacent positions. Theoretically one might find something intermediate between two faces of any crystal; however, in this work the only case of this kind observed was that of lead, intermediate between fluorite (111) and (100). It is interesting to note, too, that in case massive material is used, its position is intermediate between the positions of the faces of the crystal. The differences between two compounds are greater than the differences between two faces of the same compound; but that the latter differences exist is certain. In no case was it possible to obtain any charge from two like faces of a crystal.

When we come to a consideration of any particular case, the problem becomes more difficult. The study of the arrangement of atoms in crystals, and that of the arrangement and motions of the electrons in these atoms, have not advanced far enough to be entirely sufficient. However, with the information at present available, it is possible to explain some of the less complicated cases.

The most simple substances to consider are the elements. Every element has a definite ionization potential, that is, the amount of energy required to remove an electron from an atom is characteristic of the element. This can be calculated on the basis of its structure under the Bohr theory. In many cases this has been determined experimentally and found to agree closely with theory. There are other phenomena such as thermionic effect, and photoelectric effect which may be used as a basis for determining the "electron affinity"[1] of an element. The relative order is the same by these different methods. Taking the data that are available,[1] we find the following relations for the elements in our frictional electric series:

Element	Ion. Potential.	Electron Affinity
Ag		4.1
Cu		4.0
Zn	9.5	3.4
Pb	8.0	
Mg	7.8	2.7

The order of the elements in the frictional electric series is thus seen to correspond to the affinity for electrons indicated by other phenomena.

The so-called normal electrode potentials are also a measure of the relative tendencies of metals to lose electrons. For example, the electrode potential of Mg is more negative than that of Ag. This means that the reaction

$$Mg \longrightarrow Mg^{++} + 2\ \Theta$$

takes place more readily than

$$Ag \longrightarrow Ag^{+} + \Theta$$

and that therefore a Mg electrode will give up electrons at a greater pressure than will a Ag electrode. It does not mean, as it might seem at first, that Mg has a greater attraction for electrons than Ag has. Those atoms which actually react in each case acquire a positive charge, this occurring more easily in the case of Mg. The fact that the Mg metal which has not reacted has a more negative potential than the inert mass of the silver, is due to the greater tendency of the Mg atom to lose electrons, the reaction of course taking place continuously only when the excess electrons are removed from the electrode. The electrode potentials are therefore in accord with other phenomena depending on electron affinity.

---

[1] "Smithsonian Physical Tables," 404 (1920).

Since the conditions under which relative electron affinities are determined differ so greatly in the cases of measuring normal electrode potentials, and of arranging a frictional electric series, one should not expect that the order of a set of elements would be exactly the same in both cases. However, the agreement between the two methods is good.

In considering compounds we are dealing with atoms of more than one kind. The ease with which a surface gives up its electrons will depend on how the atoms are arranged with reference to that surface. Therefore different faces of a crystal will have differences of potential. Several examples of this fact are found in the series.

It will be interesting to consider a substance of which the crystal structure has been determined, such as fluorite,[1] CaF_2. In the (100) face the outer two layers of atoms are arranged like this:

Surface
F F F F F F F
Ca Ca Ca Ca Ca Ca

In the (111) face the arrangement has been found to be:

Surface
F F F F F F F F F

Ca Ca Ca Ca Ca Ca Ca Ca Ca

The distance between the layers is 1.73 times as great in the second case as in the first.[2] Since in the octahedron face the calcium layer is further from the surface, and also since the atoms are less exposed than in the cube face, it is to be expected that the properties of the Ca atom will be relatively more important in the (100) face than in (111).

In considering the properties of atoms in a crystal it must be remembered that the electrical structure of an atom is somewhat modified when it is part of a compound. That is, in CaF_2 the F atoms have each acquired one electron from some Ca atom, or at least are holding one in common with a Ca atom. Under such an arrangement the fluorine atom has no further tendency to take an electron from another atom; the Ca atom, having two of its electrons held by F atoms, has some tendency to take an electron if it can get one. Therefore that face, (100), in which the properties of Ca are relatively more predominant, should acquire the negative charge with reference to the other face. Experimentally, the octahedron is found to be positive with reference to the cube, as predicted.

---

[1] Bragg: "X-rays and Crystal Structure".

[2] 1.36×10^{-8} cm., and 2.35×10^{-8} cm., respectively.

Another interesting case to consider is that of a crystal in which two faces perpendicular to the same line are different. Thus in topaz, where other evidence has shown that 001 is different from $00\bar{1}$, it is found that the former charges the latter negatively. This is true either when the crystal is broken apart on its cleavage, without rubbing, or when the two faces are rubbed together. Probably when the internal structure of topaz is determined, it will be found that those atoms which more readily lose electrons are on the outside of the 001 surface, thus putting the atoms with greater attraction for electrons on the outside of $00\bar{1}$.

With two substances of different composition, the problem is more complex. If they are salts of different metals with the same acid radical, the differences are essentially those between the basic atoms themselves. Thus barite, $BaSO_4$, charges celestite, $SrSO_4$, negatively, and this charges anhydrite, $CaSO_4$, negatively. This means that the tendency to lose an electron is, greatest for Ba, and least for Ca, and is, of course, in agreement with the fact that Ca is nearer the noble elements in the electrochemical series than Ba is

In case both the acid and base are different, it may be difficult to foresee how much the effect of each will count. In general the position of a compound will be a resultant of the electron affinities of the different atoms, but the determination of the relative importance of each atom may be complex.

A thorough study of this subject would involve a consideration of various series of similar compounds, in order to determine the effects of different atoms and radicals. Such a study has not been attempted in this investigation.

However, enough has been brought out here to show that this general method of attach leads to results in accord with facts familiar to us from other phenomena. No doubt as knowledge of the electrical structure of matter increases, further consideration from this same point of view will throw more light on the subject of frictional electricity.

"Coehn's Rule"

Since Coehn's rule is perhaps the most valuable generalization of frictional electric effects that has yet been presented, it will be considered here. It states that a frictional electric series of non-conductors from positive to negative corresponds to a series from highest to lowest dielectric constant. This offers no explanation as to why the two series have the same order, why a high dielectric constant should make a substance more positive, or why good conductors occur in a frictional electric series between dielectrics. Perhaps from a consideration of the electronic theories here discussed, we can see what this rule means.

The dielectric constant of a medium is a measure of the force existing between two opposite charges in the medium. The greater the dielectric constant the less will be the force. Without attacking the problem quantitatively, we can see that, in the higher dielectric medium, an atom which is positively charged because it has lost an electron will exert a lower attractive force on an electron at the surface than will a positively charged atom in the other medium, when two non-conductors are in contact. The resultant effect will be to give the medium of lower dielectric constant a better chance to regain any electrons it may have lost, and it is therefore to be expected that it would be negatively charged. This is in agreement with the rule.

To refer the sign of charge back to the dielectric constant is really not explaining anything. Let us consider what this constant actually represents.

The arrangement of the electrical components of any medium determines its electrical properties, one of which is the dielectric constant. To say that one medium has a higher dielectric constant than another means that in the first case positive and negative charges are so arranged in its structure that an electron is attracted by a unit positive charge with a smaller force than it would be under similar conditions in the second case. The dielectric constant is merely one physical property which measures the relative attraction between an electron and the positively charged mass of the substance. In the case of conductors the methods usually applied in the determination of dielectric constants fail. The reason for this is that, since opposite charges do not persist for any appreciable time in a conducting medium, the force between such charges cannot be directly measured. Conductors, however, occur in the frictional electric series, in positions determined by their relative attraction for electrons, independent of their conducting properties.

Applications

A knowledge of the way different faces of the same crystal charge each other may be a means of giving us certain information which is more difficult to obtain by other methods.

A point brought out by this work is the possibility of using a frictional electric study to determine whether or not two faces of a crystal are alike. This method is apparently very sensitive.

For example, the two faces of gypsum parallel to the good cleavage are usually considered to be alike. However, the fact that 010 and $0\bar{1}0$ charge each other oppositely, either when a gypsum crystal is pulled apart on its cleavage plane or when the two faces are rubbed together, indicates that the two faces are different.

The Effect of Moisture

So far we have considered only ideal cases, that is, the surfaces were assumed to be clean and perfectly dry. Under ordinary conditions this is usually not true. Films of adsorbed moisture and other impurities may be present. It is well known that on damp days it is difficult to generate frictional electricity. Results so obtained are often inconsistent. Many previous investigators have had peculiar results because of this. Some were not aware of the fact that they were having any trouble; others, knowing it, cheerfully ignored it; while a few, Hoorweg for example, tried to work in the absence of moisture when it became obvious that inconsistencies were due to it. No one, up to the present, has made a systematic study of the effect of moisture, although such a study is evidently of great importance.

As a preliminary experiment, the materials previously arranged in the series were moistened by allowing steam to condense on them. On rubbing any two together, it was found that both would acquire a positive charge. This however, was small compared with the charges developed on the dry substances.

Such a method is obviously crude, and it was therefore decided to make a more careful and systematic study of a few substances. Those selected were: quartz; glass; composition insulation (CI); sealing-wax; and silver. This is a representative set, distributed throughout the series.

Five large desiccators were arranged with glass stands so that these samples could be suspended in them. The solutions in the desiccators were: (1) H_2SO_4; (2) 56% H_2SO_4, 44% H_2O; (3) 43% H_2SO_4, 57% H_2O; (4) 30% H_2SO_4, 70% H_2O; (5) H_2O. In the temperature range 15° to 25°C. these solutions will maintain aqeous vapor pressures above them in the ratio of 0%, 25%, 50%, 75%, and 100%. The relative humidities of the atmospheres in these desiccators therefore had the same relations to each other as the vapor pressures.

Specimens were placed in a desiccator and allowed to remain there for at least 24 hours to reach equilibrium. They were then rubbed on one another, and the charge measured with the electrometer. After discharging the specimen, by holding it in the ionized region near a gas flame, it was returned to the desiccator to again come to equilibrium before another determination. In this manner every possible pair of the five substances was tested at each humidity.

The results brought out the interesting fact that in every case the effect of water was the same. The exact value of the charge varied with the conditions of rubbing, but the effect of the moisture was always to add a positive charge to each surface. The naturally negative substance might be negative, neutral, or positive; the other surface was always positive.

In the extreme case where the substances had come to equilibrium with an atmosphere saturated with water vapor, the general result was to charge any two substances positively.[1] However, the two charges were not equal; the substance which would normally be negative having the lesser charge. The difference in magnitude between the two charges was quite distinct. This indicates that one effect of moisture is to add to each surface a positive charge, superimposed upon the natural tendency to charge one positively and the other negatively.

There are three factors, affecting the sign of charge, to be considered. (1) The first is the one just mentioned. Its explanation will be discussed later. (2) The contact of one solid against the water on the other will charge the solid negatively and the water positively. Similarly the second solid acquires a negative charge from the water on the other surface. These effects may be small but the result will be to leave an excess of positive charge on that surface which under normal conditions would charge positively and an equal negative charge on the other. (3) Whenever, by breaking through the moisture film, the two solids come into direct contact, they will charge according to their natural tendency, one positively, the other equally negatively.

---

[1] As will be shown later, the corresponding negative charges, which must have been generated, were acquired by the air.

The combined effect of (2) and (3) is to charge the two solids equally and oppositely. (1) adds a positive charge to both materials. The resultant will depend on the relative magnitudes of the two effects. (1) will be more predominant at higher humidities; the combined effect of (2) and (3) will increase as the two surfaces are further apart in the series.

Thus at 100% humidity the added positive effect was sufficient in all cases to overcome the other effects, and both substances were positively charged. Of course, the naturally positive substance had the greater charge.

With a relative humidity of 75% the effect due to moisture was not so great. In some cases instead of both substances being positively charged, one acquired a positive and the other a much smaller negative charge. Thus quartz and silver are near enough in the series so that the positive charge due to moisture was greater than the negative charge acquired by silver from contact with quartz; both were therefore positively charged. Similarly the CI is near enough to quartz so that both acquired a positive charge; but the difference between silver and CI is great enough to make the former charge slightly negatively.

At 50% humidity the effect due to moisture had decreased considerably. Under these conditions, the water was sufficiently important only in the cases of sealing-wax and silver, and of CI and quartz to cause both to charge positively; other pairs of substances charged unequally and oppositely.

The importance of moisture at 25% humidity was relatively small. No two substances acquired a positive charge simultaneously. The negative charges were more nearly equal to the positive charges than at higher humidities. This indicates that the natural opposite charges are greater than the positive charge added to both surfaces due to the water at this humidity.

It can readily be seen from these data that they support the previous statement: The effect of moisture is an added positive charge,[1] increasing with the humidity and decreasing as the distance in the series between substances increases.

If the effect becomes greater with the amount of water present on a surface, as would happen with increasing humidity, there must be some pairs of materials which differ so greatly in the amount of water they will adsorb at the same humidity that there will be a marked difference in the magnitude of the moisture effect. To verify this the following pairs were selected: serpentine and fur; calcite and cheesecloth; and beryl and blotting-paper. In each case the first is normally positive to the second; they are very near each other in the series; and the second is capable of much greater adsorption of moisture. These substances were allowed to come to equilibrium with water vapor and then rubbed on each other. In each case it was found that the normally negative substance of each pair, could, due to its much greater adsorption of moisture, become more positive than the other, normally positive, material.

---

[1] The corresponding negative charge is acquired by the air in contact with the film.

Since, at this point, it seemed evident that the effect of moisture must be due to the same phenomena as Lenard's "Wasserfallelektrizität",[1] it was thought desirable to see whether solutions of electrolytes behaved similarly.

It was found that if two solids were rubbed together with a 2% NaCl solution on their surfaces the previous effect was reversed, that is, a negative charge was added to each. This would lead one to expect that at some lower concentration there must be a point where the solution would not add a charge of either sign. On trying various strengths of solution with a few pairs of solids,[2] it was found that below .01 N the added charge was in the same sense as for water, while above .1 N it was the reverse. This method was not sufficiently sensitive to determine the effects between these strengths but it fixed the approximate limits within which the inversion point must lie.

A .1 N solution of HCl was also tried with these materials;[3] its presence added a negative charge to both solids.

No appreciable charges were observed on two surfaces covered with .1 N NaOH, when they were rubbed together. At normal concentration, NaOH solutions acted oppositely from water, adding a negative charge to each solid.

The facts, then, as to the effects of the presence of films of moisture, or of solutions of acid, alkali, or salts are quite simple. Water tends to add a positive charge; the others, when sufficiently concentrated, add a negative charge. The real problem, therefore, is to explain the causes of these effects.

In the case of pure water, the excess of positive charge on the substances being studied shows that negative electricity has disappeared, presumably into the air. Similarly, the solutions must have lost a positive charge to the air. This indicates that we must be dealing with another variation of a well-known phenomenon, the "Wasserfallelektrizität" of Lenard.

During the rubbing together of two solids covered with liquid films, the result is the mechanical disintegration of the films, causing the liquid to be charged electrically, the air in contact with the film acquiring an equal opposite charge.

A study of the causes of this effect is the same as an investigation of the reasons for various similar phenomena. Before discussing any further experimental work, it would be well to see what these other effects are, and what the most important researches along this line have been.

"Wasserfallelektrizität"

Although a few previous observers had noted the fact that the air near water-falls is negatively charged, it was Lenard[4] who first made a thorough study of the subject. His original paper may be said to be the basis for all further work in this field. Lenard showed that when water drops were broken up in a falls, the air was charged negatively, and the water positively. He also found that the sign of charge was the same when different gases were used. Various liquids and solutions were similarly tested. In testing NaCl solutions of different strengths, the charge of the liquid was observed to be positive up to .011% NaCl, and negative above this concentration. Lenard believed the cause of the phenomenon was a contact potential difference between liquid and gas.

---

[1] This will be discussed on p. 880.

[2] The different combinations of: topaz, glass, calcite, quartz, orthoclase, sphalerite, and silver.

[3] Calcite and sphalerite were not used because the acid would attack them.

[4] Lenard: Wied. Ann., **46**, 584 (1892).

The inverse, namely the bubbling of gas through liquids was first studied by Kelvin, MacLean, and Galt.[1] Although some of their results were incorrect, they established the fact that a gas would become charged when bubbled through a liquid, such as water, or a solution of an electrolyte.

Kösters[2] determined the charges on hydrogen and oxygen when bubbled through various liquids. In either case, the gas acquired a negative charge from water, whereas electrolyte solutions above a certain concentration charged the gas positively.

By far the most thorough work on this phase of the subject was done by Mozer.[3] In particular, hydrogen and oxygen were bubbled through quite a number of liquids and solutions of different concentrations. Qualitatively the effect of the two gases was the same. Electrolytes below a certain strength charged the gas negatively and above this the gas became positively charged. This concentration was determined for various acids, salts, and bases. It was found to be lower for acids than for their salts, while that for the corresponding base was higher. Mozer suggested that the action of an electrolyte might be due to adsorption of its ions by the gas.

Another interesting point that he brought out was the fact that a bubble of gas in a liquid is electrically charged, and with the same sign that it bears on leaving the liquid. This was shown by the motion of the bubble under an electric field.

This particular point has been the subject of several researches by McTaggart[4] who showed that an air bubble in contact with water bears a negative charge. The charges on bubbles in various solutions were tested. With $Th(NO_3)_4$ in solution the charge on the bubble could be reversed.

Numerous other workers have studied this subject. The essential facts have all been in agreement with those brought out in the papers just mentioned. The results are the same whether liquids be broken up in a gas atmosphere, or a gas be bubbled through a liquid, or even when a gas bubble is in contact with a liquid. With water the gas charges negatively, and with electrolytes above a certain strength positively; the liquid always bearing an opposite charge.

---

[1] Kelvin, MacLean, and Galt: Proc. Roy. Soc., **57**, 335 (1895).

[2] Kösters: Wied. Ann., **69**, 12 (1899).

[3] Mozer: Dissertation, Göttingen (1913); Coehn and Mozer: Ann. Physik, (4) **43**, 1048 (1914).

[4] McTaggart: Phil. Mag., **27**, 297 (1914); **28**, 367 (1914); **44**, 386 (1922).

An interesting summary of all the previous work in this field is found in an article by Becker.[1]

Lenard[2] also has summarized what was done up to 1915. According to his latest theory, the cause of electrification is not a contact potential difference, but is caused by mechanical processes, and is due to the liquid only. It is assumed that in water there exists a double layer of ions at the liquid-gas interface, the OH^- ions in the outer, and the H^+ ions in the inner layer. Electrolytes tend to have their cations on the outside, and their anions nearer the interior.

Mechanical breaking up of a drop would tear off the outer layer most readily, and the gas would acquire a charge due to the fine particles of charged liquid in it. The greater the concentration of an electrolyte, the more positive would be the outer layer of the liquid.

This explanation accounts for the charges developed by bubbling gases through liquids, or by pulverizing liquids in a gas. It does not account for the charge on bubbles, which has been definitely observed by McTaggart and others.

With this brief summary of previous work in mind, we can proceed to a consideration of the causes underlying all these similar phenomena. In the cases of bubbling, or of water-falls, it is a question of the results of disturbing conditions suddenly at a liquid-gas boundary. With bubbles in liquid, the conditions existing on the surface before anything has disturbed them are evident.

The potential difference between gas and liquid cannot be due to any strictly electrochemical process, since such chemically opposite gases as hydrogen and oxygen produce the same result, as does also the inert gas nitrogen. The fact that un-ionized organic compounds in solution do not alter the action of water appreciably, and that weak, (slightly dissociated), electrolytes do not reverse the effect as strong electrolytes do, shows that the action of substances in solutions is due to their ions. The logical conclusion is that the charge on the gas is caused by its selective adsorption of ions from the solution, the sign of charge depending on whether the positive or the negative ions are adsorbed more strongly. The existence in the gas of both positive and negative carriers of charge has been shown experimentally.[3] Most interesting is the experiment of Aselmann[4] in which he found that the gas bubbled through a NaCl solution contained both positive and negative carriers, those with positive charge containing Na, as shown by a flame test, the others being free of Na. This is exactly what would be expected on the basis of adsorption. The gas would adsorb both positive and negative ions, the concentration of the ions determining which was adsorbed more.

---

[1] Becker: Jahr. Rad., **9**, 52 (1912).

[2] Lenard: Ann. Physik, (4) **47**, 352 (1915).

[3] Bloch: Ann. Chim., **22**, 370; **23**, 28 (1911).

[4] Aselmann: Ann. Physik, (4), **19**, 960 (1906).

The process by which the gas acquires its charge is quite simple. As long as the gas and liquid are in contact, adsorptive forces hold some of the ions of the solution to molecules of the gas. The bubble in the liquid, or the gas surrounding a liquid drop or surface, will have a charge at the boundary. If then, due to some sudden mechanical disturbance, either the bubble forces its way out of the liquid, or the drops of liquid are broken into finer drops, or the liquid films on the surface of a solid are torn apart and pulverized, the gas is violently separated from the liquid, and in the process carries with it some of the adsorbed ions.

The extent to which any particular ion is adsorbed is, of course, dependent on its concentration. Although sufficient data were available to show what certain ions would do, no record had been made of the action of certain others.

For this reason it was desirable to measure the effects of various solutions not previously investigated. The method of bubbling gas through a liquid was chosen as being more accurate and convenient than that of testing solutions by rubbing them on the surface of solids. Air was used as the gas, since this is the atmosphere that is normally present in experiments. A few solutions, whose action in connection with hydrogen and oxygen had been examined by Mozer, were tried to show the comparison between air and other gases.

Experimental

In determining the charges developed by bubbling air through various liquids, use was made of apparatus very similar to that described by Coehn and Mozer. To purify the air it was passed through KOH solution to remove CO_2 and then through H_2SO_4 to dry it. The reason for removing CO_2 was to prevent changes in dilute alkaline solutions during prolonged bubbling. The purified air was then passed through a grounded copper tube containing fine brass gauze, to remove any charge it might have acquired. The solution itself was contained in a flask, this part of the apparatus being like that used by Mozer. Just above the opening of the side-arm leading from the flask was suspended a perforated platinum cone covered at theb ase with 80-mesh platinum gauze. The cone was connected to one set of quadrants of the electrometer, by means of wires insulated and shielded as described before. The cone and the flask containing the liquid were enclosed in a grounded metal container.

As gas bubbled through the liquid and went out through the side-arm it gave up the charge it acquired to the gauze, the electrometer deflection being proportional to this charge. In order to compare all the experiments on the same basis, measurement was made in each case of the change in deflection during the 15 minutes from 5 min.-20 min. after commencing the bubbling of the gas. During the first few minutes the action of the instrument was usually erratic.

Since the value of scale divisions in terms of quantity of charge may vary from day to day, a solution of .1 N $NaNO_3$ was used daily as a standard of comparison. For this reason all the results recorded are calculated with reference to the effect of .1 N $NaNO_3$ as unity.

The rate at which it is desirable to bubble the air depends on two considerations. First, if it is done too slowly, the rate of development of charge is not great enough to make measurements accurate. However, if it is too rapid, particles of liquid may be carried along and strike the gauze, causing erroneous results. The rate of flow was varied until a satisfactory speed was found. This was maintained throughout all the experiments.

Great care had to be exercised to guard against the presence of any impurities in the solutions. The smallest traces of some substances will cause results to vary greatly from their true values. For example, a very small amount of acid in a salt solution will lower the inversion concentration considerably. Therefore the flask was thoroughly rinsed several times when changing from one solution to another. Also the flask and other glassware, such as pipettes and graduates, were cleaned with bichromate-sulfuric acid mixture every day before using. In this way, it was possible to obtain consistent and reproducible results.

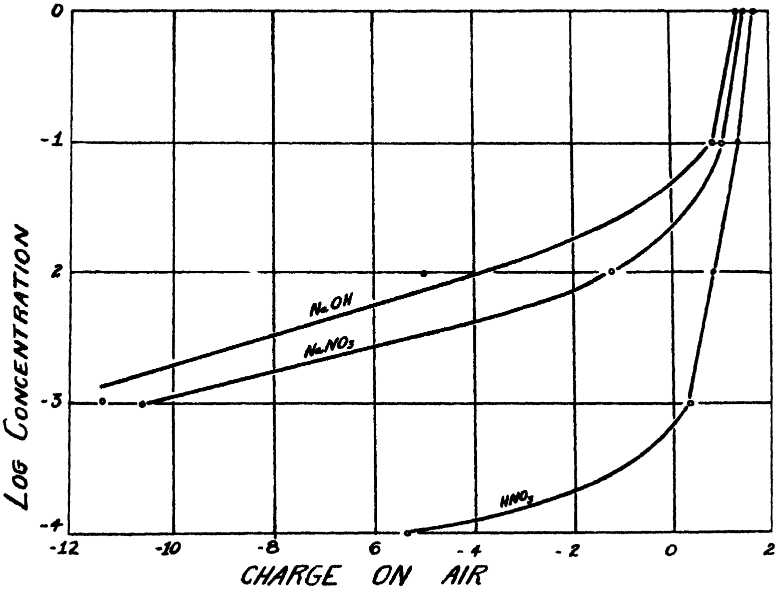


FIG. 1

Variation in Charge on Air after bubbling through Solutions NaOH, $NaNO_3$, and HNO_3.

A tabulation of the results obtained follows. The concentrations are those of ionized compound in solution, these being calculated from conductivity data. Concentrations were expressed in this manner because the object of getting the data was to show the variation in adsorption of the ions with change in their concentrations.

Determinations were usually made of the charges on the gas after bubbling through 1, .1, .01, and .001 N normal solutions. In some cases other concentrations were also found necessary. From the charges so obtained, the prob-

TABLE II
Charge on Air after bubbling through Solutions
Effect of .1 $NaNO_3$ taken as unity.

$NaNO_3$

N[1]	Charge
.001	−10.6
.01	− 1.17
.1	+ 1.00
1	+ 1.5

Inv. Conc. = .018 N

$NaOH$

N	Charge
.001	−11.3
.01	− 5.0
.1	+ 0.87
1	+ 1.45

Inv. Conc. = .031 N

$NaCl$

.001	−10
.01	− 1.3
.1	+ 0.91
1	+ 1.34

Inv. Conc. = .023 N

KOH

.001	−9.1
.01	−4.4
.1	+1.
1	+1.6

Inv. Conc. = .025 N

HNO_3

.0001	−5.3
.001	+0.34
.01	+0.80
.1	+1.32
1	+1.61

Inv. Conc. = .0003 N

HCl

.0001	−6.0
.001	+0.21
.01	+0.73
.1	+1.12
1	+1.41

Inv. Conc. = .0003 N

[2] $Th(NO_3)_4$

N	Charge
.001	−0.61
.01	+1.71
.1	+7.9

Inv. Conc. = .0015 N

$K_3Fe(CN)_6$

N	Charge
.001	−15
.01	− 6.8
.1	+ 0.41
1	+ 0.82

Inv. Conc. = .06 N

$BaCl_2$

.001	−8.1
.01	0
.1	+1.10
1	+1.54

Inv. Conc. = .01 N

* H_2O (distilled)	−150

---

[1] Concentrations refer to concentrations of ions of the substance. Thus, .119 N NaCl is about 84% dissociated, and therefore is .1 N with reference to Na and Cl ions.

[2] In the cases of $Th(NO_3)_4$ and $K_3Fe(CN)_6$, the concentrations given refer to the normality of the solution in terms of total dissolved salt, and not merely the ionized portion.

*Owing to the abnormally high value of the charge due to water, its relative value with reference to the others is only approximate.

able inversion concentration was estimated. A solution of this strength was then tested, and using the results of this with the other determinations, the inversions concentration was determined graphically. The results are given in Table II.

Three curves, showing the variation in charge on the gas with concentration of ionized HNO_3, $NaNO_3$, and NaOH are shown in Fig. 1. These compounds were chosen as examples of an acid, a salt, and a base.

Discussion

The curves shown in Fig. 1 are typical of the actions of all well-ionized electrolytes. In dilute solutions they impart to the gas a negative charge, which decreases rapidly with increasing concentration. At a definite concentration, the gas acquires no charge; above this the gas becomes positively charged, the magnitude of charge increasing only slowly with the concentration beyond this point. Mozer's curves are similar to these, although, of course, the relative values of charges at different concentrations, and the zero-point are somewhat different. This is due partly to the use of a different gas, and also to the difference in experimental conditions, such as the velocity of the gas, and the size of orifice through which it entered the solution.

The first point that strikes one on looking over the data is the relatively high negative charge due to water itself. This means that at concentrations as low as 10^{-7} the OH^- ion is adsorbed very strongly: H^+ practically not at all. (Mozer could find no positive carriers in the gas after it had bubbled through pure water). In the case of solutions of electrolytes, it is therefore to be expected that the ions of water will have an effect which will be to make the gas negative.

Let us consider some examples of solutions of electrolytes. The curves shown for HNO_3, $NaNO_3$, and NaOH are typical for acids, salts, and bases.

The action of a solution on a gas is a resultant of the combined actions of the ions of water and those of the solute. The ions of the water, as just stated, due to the much greater adsorption of the OH^- ion, tend to charge the gas negatively. The effect of the presence of the ions of the electrolyte is to change the charge in the positive direction. As the concentration of the solute increases the relative importance of the water decreases. Thus in .001 N solution the water ions are outnumbered 10,000 to 1; in 1 N solution, 10,000,000 to 1. In the latter case the water ions must play a much less important part than in the former. The charge on the gas should therefore be a resultant of a negative component, decreasing with increased concentration, and a positive component, increasing with the concentration. In examining the charge on hydrogen after bubbling through KNO_3 solutions, Mozer found the following distribution of positive and negative carriers:

Conc.	Pos.	Neg.
.001	5	50
.01	13	22
.1	15	11

The negative charge is due to the sum of the adsorption of OH^-, decreasing as the concentration of solute rises, and of the negative ion of the electrolyte, increasing with the concentration. The displacement of OH^- by another anion results in the decrease of the adsorption of negative ions. The positive charge is the resultant of the increasing adsorption of the cation, and the practically negligible adsorption of H^+, and therefore increases with the concentration. The total result is to make the charge more positive as the solution contains more of the electrolyte.

With alkalis or acids, the situation is somewhat different from the case of a salt. In alkaline solutions, the only negative ion present is the OH^- ion. The negative charge on the gas must therefore increase with the concentration. The adsorption of H^+ is negligible. As the concentration increases, the adsorption of cation may increase more rapidly than that of the OH^- ion, and at some point exceed it. This is found to be the case, but of course this concentration must be higher than that for all salts of the base in which the anion at low concentrations is less readily adsorbed than OH^-.

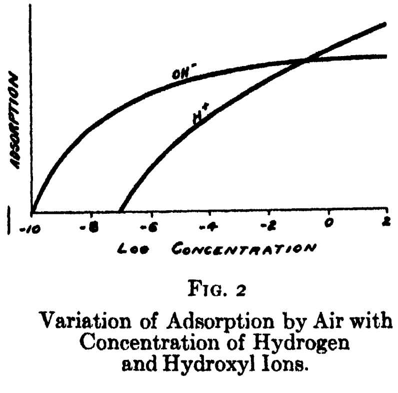


FIG. 2

Variation of Adsorption by Air with Concentration of Hydrogen and Hydroxyl Ions.

In acids the conditions are reversed. The concentration of OH^- in solutions from .0001 N up is small enough to make its adsorption of no effect. The negative charge will at all strengths of solutions be less than in the case of salts of the acid, but it will increase with the concentration. The inversion point for acids will therefore occur at lower concentrations than are necessary for salts of the acid. It should be noted, however, that this would not necessarily be due to the adsorption of H^+ being greater than that of other positive ions, but might be due essentially to the decreased negative effect of OH^- ions in acid solutions.

It may be well to point out why the difference between the inversion point for acids and that for salts is so much greater than the difference between inversion points of salts and bases. For examples these concentrations are for HNO_3 .0003 N, for $NaNO_3$ .018 N, and for NaOH .031 N. When we consider the probable relations between adsorption and concentration for both the OH^- and the H^+ ion, the reason is apparent.

The data indicate that the adsorption isotherms for these two ions are qualitatively as shown in Fig. 2.

This is based on the assumption that at a concentration of 10^{-7}, OH^- has reached nearly its maximum of adsorption, this increasing very slowly beyond this concentration. H^+ at a concentration of 10^{-7} is practically not adsorbed at all. The evidence is that at normal concentration the hydrogen ion is adsorbed more than the hydroxyl ion.

It will be obvious that while in acid solutions the effect of the otherwise strongly adsorbed OH^- is cut down very much, and the effect of H^+ increased considerably above its value at 10^{-7} concentration, in alkaline solutions the increase in OH^- adsorption is not so great, and the effect due to removing the already negligible H^+ is nothing. Hence the acid inversion point should be much further below that of the salt, than the latter is below the alkali zero-point.

The question may arise as to why the OH^- ion of the water is considered as having any effect in a salt solution where other anions are present in so much greater number. The large negative charge due to pure water shows that the adsorption of the hydroxyl ion is enormous in concentrations as low as 10^{-7}. So although in a salt solution there are many more negative ions present, trying to be adsorbed by the gas, the OH^- ions are much better at it, and will therefore have an appreciable effect. Of course, the greater the concentration of the salt, the more will its anions displace the OH^- ion.

Some other interesting information can be obtained from these data. For example, $BaCl_2$ changes its action at .01 N, whereas NaCl must be .023 N before it changes. This means that the divalent Ba^{++} ion is adsorbed more strongly than the monovalent Na^+. Also the tetravalent Th^{++++} is even much more effective, showing that it is very strongly adsorbed. This indicates increasing adsorption with increase in valence.

On the other hand, the trivalent anion $Fe(CN)_6^{---}$ is even more strongly adsorbed than OH^- and therefore the inversion for $K_3Fe(CN)_6$ is higher than for KOH.

It is reasonable to assume that in normal concentration the effect due to the ions of water does not amount to much, and that therefore the relative charges give a measure of the relative adsorptions of the various ions. On this basis we find that the order of adsorption from greatest to least is:

Th^{++++}, H^+, Ba^{++}, K^+, Na^+, $Fe(CN)_6^{---}$, OH^-, Cl^-, NO_3^-.

Applications to Frictional Electricity

One of the objects of this investigation has been to see how the observed effects of moisture account for anomalies previously observed. It is evident that since certain films on the surface of a solid tend to add a negative charge while others tend to add a positive one, the possible variations of effects are many.

For example, the normally positive surface might have on it a film which would acquire a negative charge, while the other substance was covered with a film tending to become positive. The results obtained in this case would vary with the extent to which the two solids were rubbed together. No doubt much of the confusion in the past has been due to effects of this nature.

To consider an actual case, Shaw found that mica when beaten lightly on glass became positively charged, when it should have become negative. When rubbed firmly the mica charged negatively. This is what would be expected if the mica, (which has a strong tendency to adsorb moisture), were wet. If a clean, dried mica surface be used, it becomes negatively charged even if only rubbed lightly.

In some experiments on sand, Phillips[1] found that if it were allowed to slide over a filter paper, the paper charged positively when it should charge negatively. He explained this on the basis that sharp edges of sand will charge the paper positively, while dull surfaces of sand would cause a negative charge. There is no apparent reason why the paper in this experiment came into contact mainly with the sharp edges of the sand. It is interesting to note that Phillips considered moistness of the paper a prerequisite for the experiment.[2] It is to be expected that if the paper were sufficiently moist, it would acquire a positive charge when rubbed by the sand. His experiment has however not been repeated here.

During a previous investigation,[3] carried out in this laboratory, some unusual effects were noted when gases were bubbled over metal electrodes in acid solutions.

It was found that, using oxygen on one of two copper electrodes, the aerated one was anode, contrary to expectations. Iron or nickel electrodes acted as they should; they were cathode when oxygen was bubbled over them. One should also have expected that hydrogen would reverse the results, but actually it acted in exactly the same way as oxygen; copper was anode, and iron or nickel cathode when the gas was bubbled over them. Similar results were obtained with nitrogen, air, illuminating gas, and carbon dioxide.

No attempt will be made here to explain why copper acts differently from iron and nickel. But the point of interest is that the charge producing these effects must be due to the same phenomenon that we are discussing here; namely the charge acquired by a gas due to selective adsorption of the ions of a solution.

This indicates at once that the potential of a gas electrode may be affected somewhat by this action. In a recent paper by Arkadjev,[4] it is shown that the potential of a hydrogen electrode with reference to a .1 N HBr solution is increased, that is, made more positive, by the addition to the solution of a neutral salt.

With KNO_3 and KCl the lowest concentrations made the electrode more negative; then with increasing concentration it became more positive. With NaCl, LiCl, KBr, and LiBr, the action was to make the electrode more positive with greater concentration.

It seems reasonable that these results are due, at least in part, to the adsorption phenomena discussed in this paper.

---

[1] Phillips: Proc. Roy. Inst., 19, 742 (1910).

[2] "I need hardly point out that the filter paper used should not be specially dried. Pieces which have been left about in a room for a few hours adsorb sufficient moisture to insure the right degree of conductivity."

[3] Bancroft: J. Phys. Chem., 28, 842 (1924).

[4] Arkadjev: Z. physik. Chem., 104, 192 (1923).

In this study of the effect of moisture, certain anomalies observed by previous workers have been explained; and the possible explanation of others not discussed is thereby suggested. The necessity of working in the absence of moisture, if reproducible results are desired, is apparent.

Summary

The results of this investigation have been the following:

1. A frictional electric series has been established, including several substances not previously placed, and showing the effect of using different crystal faces.
2. An explanation of frictional electricity has been proposed, using the electronic structure of matter as a basis.
3. A suggestion as to the physical significance of "Coehn's rule" has been offered.
4. The effect of moisture films on frictional electric charges has been shown to be related to Lenard's "Wasserfallelektrizität".
5. The charges produced when air is bubbled through various solutions have been measured.
6. An explanation of these effects, (4 and 5), has been presented on the basis of the selective adsorption of ions by a gas.

The writer wishes to express his sincere appreciation to Professor W. D. Bancroft, under whose direction this investigation was carried out, for his valuable criticisms and helpful suggestions.

Cornell University.

IONISATION BY RADON IN SPHERICAL VESSELS

BY W. MUND

In quantitative work on the chemical effects of α rays, it is found very convenient to mix a given amount of radon with the homogeneous system to be studied. Very often one wishes to know the number of pairs of ions which are formed in the reaction vessel.

In a liquid the range of α rays is so small that adsorption by the walls of the vessel may be disregarded. In a gaseous mixture the loss of ionisation that occurs through many particles encountering the glass has to be taken into account.

This problem was solved by S. C. Lind[1] for small spherical bulbs having diameters about half the range of the α particles from radon.

Ionisation per unit length of path varies for an α ray with the distance r − x, from the end point of the range. According to Geiger's law it is expressed by

$$i = k(r - x)^{\frac{1}{3}}$$

From this relation it may be shown that for values of x not exceeding 2 or 3 cms the α particle leaves on its track a number of ions very nearly proportional to x. Assuming this simplification S. C. Lind has been able to calculate the ionisation in small spheres.

The following results may be looked upon as a further step in the direction opened by Lind.

Two assumptions have been found necessary:

1. The validity of Geiger's law.

2. That all the Ra A and Ra C as soon as formed in the bulb is deposited on the walls.

If these points are granted the merely mathematical problem is solved in two steps without any further simplification.

I. Let N_o atoms of radon be uniformly spread in a sphere of radius R; let r be the range of every α particle emitted by the radon; and $k\,r^{\frac{2}{3}}$ the number of pairs of ions which the particle would produce if not stopped by the wall. The total number of pairs of ions formed during the time t is given by:

$$I_1 = N_o(1 - e^{-\lambda t})kr^{\frac{2}{3}}\left[1 - \frac{9}{20}\frac{r}{R} + \frac{81}{3520}\left\{\left(\frac{r}{R}\right)^3 + \left(1 - \frac{2R}{r}\right)^{\frac{5}{3}}\left(\frac{32}{3}\frac{r}{R} - \frac{10}{3}\frac{r^2}{R^2} - \frac{r^3}{R^3}\right)\right\}\right]$$

In this formula the difference r − 2R is supposed to be positive; if 2R > r, a much simpler formula is obtained:

$$I_1 = N_o(1 - e^{-\lambda t})kr^{\frac{2}{3}}\left\{1 - \frac{9}{20}\frac{r}{R} + \frac{81}{3520}\left(\frac{r}{R}\right)^3\right\} \qquad (2)$$

---

[1] S. C. Lind: "The Chemical Effects of Particles and Electrons", 82 (1921).

II. Let equilibria amounts of Ra A be spread on the walls of the vessel corresponding to the initial number N_o of atoms of radon. Let r′ be the range of α particles from Ra A. The total ionisation is given by:

$$I_2 = N_o(1 - e^{-\lambda t})kr'^{2/3}\left\{\frac{1}{2} - \frac{3}{20}\frac{r'}{R} + \frac{3}{20}\left(1 - \frac{2R}{r}\right)^{2/3}\frac{(r' - 2R)}{R}\right\} \qquad (3)$$

A similar formula applies to ionisation, I_3 from Ra C, r″ being the range of particles, from this source.

Again $r' - 2R$ and $r'' - 2R$ are supposed to be positive. If they are not the formula becomes:

$$I_2 = N_o(1 - e^{-\lambda t})kr'^{2/3}\left(\frac{1}{2} - \frac{3}{20}\frac{r'}{R}\right) \qquad (4)$$

The mathematical argument leading to formulas (1), (2), (3) and (4) is fully developed in an earlier (French) paper[1]. It may be briefly outlined thus:

Consider a surface element of area *ds* on the wall of the spherical vessel. Using Geiger's law the loss of ionisation is calculated which occurs through α rays striking *ds*. The double integration takes into account the α rays of every direction and from every distance compatible with the radius R, the ranges r, r′ and r″ and the distribution of the radiating source.

The formulas referring to radon Ra A and Ra C must be combined in different ways according to the size of the vessel:

1. In small spheres ($2R < r$) the total ionisation is expressed by

$$I = I_1 + I_2 + I_3 = N_o(1 - e^{-\lambda t})kr^{2/3}\,F \qquad (5)$$

Putting $r'/r = a$, $r''/r = b$ and $r/R = \rho$ the function F is given by:

$$F = 1 + \tfrac{1}{2}a^{2/3} + \tfrac{1}{2}b^{2/3} - \frac{3}{20}\rho\left\{3 + a^{5/3} + b^{5/3} - \left(a - \frac{2}{\rho}\right)^{5/3} - \left(b - \frac{2}{\rho}\right)^{5/3}\right\} \qquad (6)$$
$$+ \frac{f1}{3520}\left\{\rho^3 + \left(1 - \frac{2}{\rho}\right)^{5/3}\left(\frac{32}{3}\rho - \frac{10}{3}\rho^2 - \rho^3\right)\right\}$$

Assuming for *a* and *b* the numerical values

$$a = \frac{4.50}{3.94} = 1.142;\ b = \frac{6.57}{3.94} = 1.667$$

Formula (6) may be written:

$$F = 2.249 - 0.989\rho + 0.15\rho\left\{\left(1.142 - \frac{2}{\rho}\right)^{5/3} + \left(1.667 - \frac{2}{\rho}\right)^{5/3}\right\}$$
$$+ 0.02301\left\{\rho^3 + \left(1 - \frac{2}{\rho}\right)^{5/3}\left(\frac{32}{3}\rho - \frac{10}{3}\rho^2 - \rho^3\right)\right\} \qquad (a)$$

---

[1] Ann. Soc. Scient. Bruxelles, **44**, 336. The expression (I) given in the present text is identical with formula (16) on p. 344 of my former paper. Being a somewhat simpler form of the same relation it should be preferred in numerical calculations. Another identical expression has been kindly brought to my notice by Dr. D. C. Bardwell.

2. If $2 > \rho > 2/1.142 = 1.75$

$$F = 2.249 - 0.989\rho + 0.15\rho\left\{\left(1.142 - \frac{2}{\rho}\right)^{5/3} + \left(1.667 - \frac{2}{\rho}\right)^{5/3}\right\} + 0.02301\rho^3 \quad \text{(b)}$$

3. If $1.75 > \rho > 2/1.667 = 1.2$

$$F = 2.249 - 0.989\rho + 0.15\rho\left(1.667 - \frac{2}{\rho}\right)^{5/3} + 0.023\rho^3 \quad \text{(c)}$$

4. If $1.2 > \rho$

$$F = 2.249 - 0.989\rho + 0.023\rho^3$$

The calculations may be avoided by plotting a curve from the following tables:

Formula (a)

From $\rho = \propto$ to $\rho = 2.0$

ρ	F	ρF
oo	0.000	——
10.0	0.111	1.110
5.0	0.226	1.130
4.0	0.287	1.148
3.0	0.391	1.173
2.5	0.480	1.200
2.4	0.504	1.209
2.3	0.530	1.218
2.2	0.556	1.224
2.1	0.587	1.232

Formula (b)

From $\rho = 2$ to $\rho = 1.75$

ρ	F	ρF
2.0	0.621	1.241
1.9	0.659	1.252
1.8	0.706	1.270

Formula (c)

From $\rho = 1.75$ to $\rho = 1.2$

ρ	F	ρF
1.75	0.731	1.279
1.7	0.759	1.290
1.6	0.817	1.307
1.5	0.880	1.320
1.4	0.946	1.324
1.3	1.020	1.326
....		

Formula (d)

From $\rho = 1.2$ to $\rho = 0$

ρ	F	ρF
1.2	1.101	1.321
1.1	1.191	1.310
1.0	1.283	1.283
0.9	1.376	1.238
0.8	1.470	1.176
0.7	1.565	1.095
0.6	1.661	0.997
0.5	1.757	0.878
0.4	1.855	0.742
0.3	1.953	0.586
0.2	2.051	0.410
0.1	2.150	0.215
0.0	2.249	0.000

In using these tables the ratio $\rho = r/R$ must be known, r is easily found when the specific ionisation s of the gaseous mixture is given. It is then expressed by the relation.

$$r = \frac{3.94}{s} \cdot \frac{76}{P} \cdot \frac{273 + t}{273} \quad (7)$$

The product ρF tabulated in the third column becomes nearly constant for values of ρ increasing beyond 3.

Between $\rho = 3$ and $\rho = 1.75$ the error that would be made on assuming ρF to be constant and equal to its limiting value of about 1.10, never exceeds 20% and vanishes again for $\rho = 1.75$. This approximative constancy of ρF for large values of ρ means that in small bulbs the ionisation is almost proportional to the pressure P

$$I = KP \tag{8}$$

For large diameters or pressures, on the contrary, ρ^3 becomes negligible and the ionisation formula (d) may be further simplified

$$I = N_o(1 - e^{-\lambda t})kr^{2/3}(2.249 - 0.989\, r/R)$$

or

$$I = I_\alpha(1 - A/RP) \tag{9}$$

Where

$$I_\alpha = N_o(1 - e^{-\lambda t})k\rho^{2/3} \times 2.249$$

and

$$A = \frac{0.989}{2.249} \times 3.94 \times 76 \times \frac{(273 \times t)}{273} \times \frac{1}{s}$$

For air at 76 cm and 15°C

$$A = 138.84 \text{ and } I_\alpha = N_o(1 - e^{-\lambda t})1.69 \times 10^5 \times 2.249$$

Let C be the quantity of radon in curies. The ionisation for the duration of one second will be:

$$dI/dt = C \times 3.72 \times 10^{10} \times 1.69 \times 10^5 \times 2.249\,(1 - 138.8/RP)$$

$$dI/dt = C \times 14.7 \times 10^{15}(1 - 138.8/RP) \tag{10}$$

This allows a comparison with the empirical formula of Duane and Laborde[1] for cylindrical vessels at 15°C:

$$I_{max} = X \times 13.5(1 - 0.572\, S/V)$$

I_{max} is the saturation current in electrostatic units. If 4.77×10^{-10} E.S.U. is the charge of every ion

$$I_{max} = dI/dt \times 4.77 \times 10^{-10}$$

X is the quantity of radon expressed in gram-seconds of Ra

$$X = \frac{1.77 \times 10^{16}}{3.72 \times 10^{10}}\, C = 4.75 \times 10^5 C$$

S is the surface and V is the volume of the vessel. If the formula of Duane and Laborde were to be tested in the case of a spherical vessel, we would write.

$$\frac{S}{V} = \frac{4\pi R^2}{4/3\, \pi R^3} = \frac{3}{R}$$

and

$$dI/dt \times 4.77 \times 10^{-10} = C \times 4.75 \times 10^5 \times 13.5(1 - 1.716/R$$

For a pressure $P = 76$

$$dI/dt = C \times 13.6 \times 10^{15}\,(1 - 130.4/RP)$$

---

[1] Le Radium, 7, 162 (1910).

So there is found a fair agreement between the theoretical and the empirical ionisation formula though the latter originated from measurements on cylindrical vessels. This supports the statement made by Lind that the ionisation in a cylindrical tube may be put approximately equal to the ionisation in a spherical bulb of the same volume.

Though nothing very definite is known on the mechanism of radiochemical reactions, it is quite possible that in several cases the intensity of chemical effects varies along the path of the α particle according to the same law as intensity of ionisation. If this could be proved to be true, the function F which expresses from the stand-point of ionisation the utilisation coefficient of the radon, would hold for chemical action as well.

As a matter of fact, the simplified formula 8 has worked quite satisfactorily in expressing Lind's results[1] on the radiochemical water synthesis as well as one single result of those of Scheuer[2], Formula (9) is identical with the empirical law that Wourtzel[3] has deduced from his very careful measurements on the decomposition of H_2S by means of radon[4]. Recently the formulas (d), (c) and (b) have yielded a constant ratio M/I in studying the radiochemical condensation of acetylene[5]. Nevertheless it must be admitted that the available data are scarcely accurate enough to settle the question.

Summary

Assuming Geiger's law, formulas and numerical tables are given for the calculation of the number of ions which are produced in a spherical vessel by the α rays of a given amount of radon in equilibrium with Ra A and Ra C wholly deposited on the walls.

Louvain
March, 1926.

---

[1] S. C. Lind: J. Am. Chem. Soc., **41**, 531 (1919).

[2] O. Scheuer: Compt. rend. **159**, 423 (1914).

[3] E. Wourtzel: Le Radium, **2**, 289 (1919).

[4] Wourtzel's formula: $M = M_\infty(1 - A/RP)$ was used by him to calculate by extrapolation the amount of chemical reaction per curie of radon in a bulb of infinite radius. He assumed that, at infinite radius, RaA and RaC would not reach the walls and that therefore the alpha radiation would be utilized completely. Thus $I_\infty = N_0(1 - e^{-\lambda t})(1.69 + 1.84 + 2.37)10^5$. By equation above $I_\infty = N_0(1 - e^{-\lambda t})1.69 \times 10^5 \times 2.249$. The value taken by Wourtzel for I_∞ is therefore 1.55 times that arrived at by equation 9.

[5] W. Mund and W. Koch: Bull Soc. chim. belg. **34**, 241 (1925); J. Phys. Chem., **30**, 289 (1926).

THE FORMATION OF CARBON DIOXIDE FROM ALCOHOLS*

BY WILBUR A. LAZIER AND HOMER ADKINS

The production of small amounts of carbon dioxide from ethanol, over various oxide catalysts, along with the main reactions of dehydrogenation or dehydration has been reported by several investigators and various attempts have been made to explain its formation. Brown and Reid[1] have suggested two possible explanations. According to the first, the aldehyde formed by dehydrogenation may condense to the ester which on decarboxylation would yield carbon dioxide. The other explanation depends upon the rupture of the aldehyde and the production of elementary carbon and carbon dioxide from the resulting carbon monoxide. The latter idea has been carried over from the work of Sabatier on the effect of nickel on aldehydes and has been applied to oxide catalysts. There is a possibility that carbon dioxide might also be produced thru the reaction of carbon monoxide with water, i.e., thru the "water gas reaction". Pease and Yung[2] reported that no carbon dioxide was produced by alumina provided air was excluded from the catalyst. Adkins believes that over the temperature range studied by Pease and Yung, no carbon dioxide is produced from a sufficiently pure alumina catalyst, regardless of whether air is adsorbed on the catalyst or not.

In view of the experience gained in this laboratory it is believed that none of these explanations are adequate to explain the facts in the case of alcohols other than methanol. No products of the decarboxylation of esters other than carbon dioxide have been found among the products of the reaction of ethanol over zinc oxide. No methane has been found, therefore excluding the possibility of a splitting up of acetaldehyde into carbon monoxide and methane. Also the amount of carbon deposited on the catalyst is entirely inadequate to account for the formation of carbon dioxide from the monoxide. It will be necessary, before presenting an explanation of the reaction, to review some of the facts reported elsewhere and also to present some new data bearing on this question.

Dr. Bischoff, in this laboratory, has noted the formation of 1.5 to 3.5% of carbon dioxide in the gases produced by ethanol over titania at 430°. Under the same conditions butanol produced from 1 to 2%. A brown water-insoluble unsaturated resinous substance was always found. The same observation has been made with zinc oxide as a catalyst and 5% or more of carbon dioxide may be produced from ethanol by the zinc oxide from zinc isopropoxide. It has been shown that this property of the catalyst is also dependent upon the method of preparation, for zinc oxide from the hydroxide yields less than 1% of carbon dioxide.

---

*Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin.

[1] J. Phys. Chem., **28**, 1081 (1921).

[2] J. Am. Chem. Soc., **46**, 390 (1924).

It has been noted that there is an important relation between the amount of resinous material in the distillate and the volume of carbon dioxide produced. Acetaldehyde which gave 40% of carbon dioxide over precipitated iron oxide at 400°, produced a very dark distillate containing several cc. of the insoluble resin, while reduced nickel, which produced no carbon dioxide, gave a distillate that was almost water-white. All of the samples of zinc oxide produced varying amounts of carbon dioxide from acetaldehyde and in every case the resin formation was of the same relative magnitude as the formation of this gas. Another constant characteristic of the reactions of alcohols at the surface of oxide catalysts is the production of a low acidity in the distillate.

The effect of various factors upon the carbon dioxide and acid productions over zinc oxide catalysts has been observed. The factors considered are: 1. the depth of the catalyst bed, 2. the presence of water in the alcohol, 3. the temperature of reaction, 4. the previous heat treatment of the catalyst, and 5. the structure of the alcohol. The experimental methods were those previously described[1]. The data are summarized in Table I. The "acidity" referred to in the last column of the table is that of the distillate (for one hour) and is expressed in terms of the number of cc. of 0.4 N alkali necessary for its neutralization, carbon dioxide having been removed.

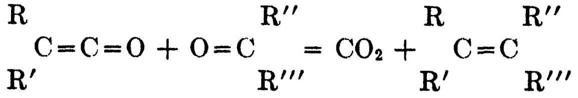
Certain conclusions may be drawn from these data. 1. The production of carbon dioxide was not dependent on the depth of the catalyst bed although the production of acid was slightly affected by this factor. 2. Water in the alcohol cut down the total activity and decreased the proportion of ethylene while increasing the proportion of carbon dioxide and hydrogen. There also was formed a small amount of saturated hydrocarbons in the runs in which the alcohol was diluted with water. The degree of acidity developed was increased by the water. 3. An increase in the temperature of reaction increased the proportion of carbon dioxide formed. 4. Heat treatments of the catalyst lowered the total activity but affected carbon dioxide production to a still greater extent. 5. Carbon dioxide production was decreased with increase in molecular weight of the alcohol and was almost nil in the case of secondary alcohols.

It is believed that the formation of carbon dioxide can be best explained by assuming the dehydrogenation of acetaldehyde. We are familiar with the conversion of acetone into ketene[1] at the surface of clay plate at 650°. This reaction consists of removing a molecule of methane from the acetone molecule leaving ketene. The position of the equilibrium is very favorable for this reaction and therefore the two products are obtained after cooling. Assuming that aldehydes are capable of dehydrogenation, ketenes should also be formed from these compounds; but hydrogen reacts with ketene at room temperature to regenerate the aldehyde so no ketene is obtained. This reaction is extremely rapid so that the ketene is immediately combined with hydrogen as soon as the reaction mixture is cooled. But the ketene may also react with water or aldehyde. The formation of acetic acid would result from the reaction with water. It is known that the following reaction takes place between aldehydes and ketones and ketenes:

---

[1] Lazier and Adkins: J. Am. Chem. Soc., **47**, 1719 (1925).

[1] Schmidlin and Bergman: Ber., **43**, 2821 (1910).



$$\underset{R'}{\overset{R}{}}C{=}C{=}O + O{=}C\underset{R'''}{\overset{R''}{}} = CO_2 + \underset{R'}{\overset{R}{}}C{=}C\underset{R'''}{\overset{R''}{}}$$

TABLE I

Ethanol at 425° over various weights of zinc oxide ("Dry Process")*

g. of ZnO	l gas per hr.	$\%CO_2$	$\%C_NH_{2N}$	$\%H_2$	"Acidity"
2	2.0	1.0	13.0	86.0	0.4
5	3.2	1.0	15.0	84.0	1.0
10	5.3	1.5	14.5	84.0	2.0
Ethanol + water at 425° over 1 g. zinc oxide (Ex-isopropoxide)					
%water in alcohol					
0%	3.9	3.5	18.0	78.5	1.1
27.5%	1.6	6.6	7.0	82.5†	5.3
38.8%	1.3	7.0	6.4	84.8†	5.9
Ethanol over 2 g. zinc oxide ("Dry Process")					
Temp.					
350°	1.3	1.0	10.0	89.0	—
400°	3.2	3.5	12.0	84.5	—
450°	5.4	6.5	10.0	83.5	—
Ethanol over 1 g. zinc oxide (Ex-isopropoxide) previously heated					
Heat Treatment					
4 hrs. at 650°	0.2	—	—	—	0.0
2 hrs. at 500°	2.3	0.9	22.0	77.1	0.6
None	3.9	3.5	18.0	78.5	1.1
Various alcohols over 1 g. zinc oxide (Ex-isopropoxide) at 450°					
Ethanol	—	5.0	19.0	76.0	—
Propanol	—	4.2	2.0	93.8	—
Butanol	—	1.7	3.5	94.8	—
iso-Butanol	—	1.4	1.0	97.6	—
iso-Propanol	—	0.4	6.9	92.7	—

* This sample of zinc oxide was a high grade commercial product.

† One or two % saturated hydrocarbons were present.

The expected reaction between an adsorbed ketene molecule and an adjacent molecule of an aldehyde would yield carbon dioxide and an unsaturated hydrocarbon. High temperature favors the polymerization of these highly unsaturated radicals, especially in the presence of ketene which is itself readily polymerized, so instead of the low boiling hydrocarbons the resinous material observed in the experiments is obtained. It is interesting to note that Hurd and Kocour[1] during the preparation of ketene obtained resins in their distillates having the same general properties as those noted above.

The presence of acetic acid in the distillates is explained by the reaction of the adsorbed ketene molecules with water molecules from water originally in the alcohol or from that formed by the dehydration reaction. It has been shown that water in the alcohol favors this reaction but at the same time cuts down the other reactions.

The difficulty of formation of the higher ketenes is evidenced by the negative results which have been reported (Hurd and Kocour, above reference) and there has been less carbon dioxide observed with the higher alcohols. Since ketones are much less reactive than aldehydes, the temperature range studied for the alcohols is too low to allow the splitting off of methane from acetone and so no carbon dioxide is produced from isopropyl alcohol. Little more than a trace of carbon dioxide has been observed in experiments with this alcohol.

The reaction in which carbon dioxide is formed is not secondary in that the acetaldehyde formed at one point is adsorbed at another to undergo this reaction, for if such was the case, a larger amount of catalyst should give a higher proportion of carbon dioxide which has been shown to be contrary to fact. The reaction is only secondary in the sense that a molecule of aldehyde formed by dehydrogenation of the alcohol, instead of leaving the catalyst undergoes another dehydrogenation to form an adsorbed molecule of ketene which may then react with its neighboring molecules.

Madison,
Wisconsin.

---

[1] J. Am. Chem. Soc., **45**, 2170 (1923).

THE THERMAL DECOMPOSITION OF METHANE. II

BY R. C. CANTELO

The equation $CH_4 \rightleftharpoons C + 2H_2$ accurately expresses the methane equilibrium[1]. It is evident from this that the rate of decomposition of methane is proportional to the concentration of methane at any instant; while the reverse reaction proceeds at a rate proportional to the square of the concentration of hydrogen.

In the following treatment

x = decrease in partial pressure of methane at time t.

x_α = decrease in partial pressure of methane when $t = \propto$ i.e. when equilibrium has been reached.

The following table is then self-explanatory.

TABLE I

Time	Partial Pressures	
	$CH_4 \rightleftharpoons$	$C + 2H_2$
o	a	b
t	$a - x$	$b + 2x$
t_α	$a - x_\alpha$	$b + 2x_\alpha$

Then $d(b + 2x)/dt = k_1(a - x) - k_2(b + 2x)^2$

$$2\ dx/dt = k_1(a - x) - k_2(b + 2x)^2$$

At equilibrium $0 = k_1(a - x_\alpha) - k_2(b + 2x_\alpha)^2$

Subtracting
$$\begin{aligned} 2\ dx/dt &= k_1(x_\alpha - x) + 4k_2[b(x_\alpha - x) + (x^2_\alpha - x^2)] \\ &= (x_\alpha - x)\,[k_1 + 4k_2(b + x_\alpha + x)] \\ &= 4k_2(x_\alpha - x)\,[k_1/4k_2 + b + x_\alpha + x] \end{aligned}$$

But $k_1/k_2 = \overline{K} = p^2_{H_2}/p_{CH_4}$

$\therefore\quad dx/dt = 2k_2(x_\alpha - x)\,[\overline{K}/4 + b + x_\alpha + x]$

Put $[\overline{K}/4 + b + x_\alpha] = B$.

Then $dx/dt = 2k_2(x_\alpha - x)\,(x + B)$.

$$dx/(x_\alpha - x)\,(x + B) = 2k_2dt$$

which integrated and the constant of integration added gives

$\ln\,(x + B)/(x_\alpha + x) - \ln\,B/x_\alpha = 2k_2(x_\alpha + B)t$ or

$\log\ (x + B)/(x_\alpha - x) - \log\,B/x_\alpha = 2k_2(x_\alpha + B)t \times 0.4343$

$\log\ (x + B)/(x_\alpha - x) - \log\,B/x_\alpha = 0.8686\ k_2(x_\alpha + B)t$ (Eq. 1)

from which k_2 can be determined for any value of t, when x and x_α are known.

The meaning of x and of x_α requires careful consideration. These are changes in the partial pressure of methane, respectively at time t and when equilibrium has been reached.

From the equation $CH_4 \rightleftharpoons C + 2H_2$, it is evident that when the partial pressure of methane has decreased by x the total pressure has become $1 + x$. Thus x and x_α are not values measured under atmospheric pressure but under a pressure of $1 + x$ atmospheres. It is usual, however, in experimental work to allow the volume to change while the pressure is kept constant at one atmosphere. The partial pressures obtained under these conditions are obviously such that the total pressure is one atmosphere. Yet the values of x and x_α can be calculated from analytical data for atmospheric pressure. The "physical" correction for the partial pressure of hydrogen determined under a total pressure of one atmosphere is given by the equation $2x_\alpha/(1+x_\alpha) = p_{H_2}$, but in addition it is necessary strictly to apply a "chemical" correction as well. This will be apparent from the following concrete example.

---

[1] Bone and Coward: J. Chem. Soc., **93**, 1197 (1908); Mayer and Altmayer: Ber. **40**, 2134 (1907); Coward and Wilson: J. Chem. Soc., **115**, 1380 (1919).

For 1000°C., the equilibrium concentration of hydrogen, calculated by the method given below, is 0.98 atmospheres.

$$2x_\alpha/(1 + x_\alpha) = 0.98, \text{ whence } x_\alpha = 0.96,$$

i.e. the partial pressures of hydrogen and methane respectively are 1.92 and 0.04 atmospheres under a total pressure of 1.96 atmospheres.

But $p^2_{H_2}/p_{CH_4} = K_p$; and it is evident that the value of the expression on the left hand side of the equation tends to increase, assuming no reaction to take place. Therefore, to restore the equilibrium ratio K_p, combination of hydrogen with carbon must occur to form methane. In the present example, let y = this decrease in partial pressure of hydrogen. Then

$$\frac{(1.92 - y)^2}{(.04 + y)} = K_p = 55.5 \text{ (for 1000°C.)}$$

y by trial is found to be between 0.02 and 0.03. Since, however, the value 0.98 calculated for the equilibrium concentration of hydrogen is itself in error 3% at least, the refinement obtained by applying this second correction (in itself strictly accurate) would be solely imaginary. The writer has therefore used the expression

$$2x_\alpha/(1 - x_\alpha) = p_{H_2}$$

as a first approximation to determine x_α. In the case of the determination of x, the "physical" correction is the only one that can be applied.

It is possible now to test Equation 1 by data for 985°C., given by Bone and Coward[1]. Table II gives the results of a series of experiments in which methane was shut up in heated tubes (unpacked) at atmospheric pressure for different periods of time.

TABLE II

Temperature	985	985	1000	985	985
Time in minutes	1	5	15	30	60
C_2H_2	0.5	0.5	nil	nil	nil
C_2H_4	0.3	0.5	1.3	0.3	nil
CH_4	90.4	75.4	65.25	61.85	48.2
H_2	8.8	23.6	33.3	38.8	51.2

For purposes of calculation we can call the temperature 1000°C., and it is necessary now to determine K_p and x_α for this temperature.

Saunders[2] develops the following equation for the equilibrium constant for the reaction between methane, hydrogen and *amorphous* carbon:

---

[1] J. Chem. Soc., **93**, 1197 (1908).

[2] J. Phys. Chem., **28**, 1151 (1924).

$$\log K_p = 4{,}583/T - 1.75 \log T + 0.000630\, T - 0.7$$

and shows that this gives results in agreement with Mayer and Altmayer's[1] determined constants. For $T = 1273°K.$ this gives $K_p = 55.5$, from which the equilibrium values of hydrogen and methane can be obtained by the method given by the writer in a previous paper[2], $p_{H_2} = 0.98$, whence $x_\alpha = 0.96$. Again in this series of experiments $b = 0$, so that $B = 55.5/4 + .96 = 14.86$.

It is necessary now to calculate the values of x corresponding to the analytical data of Table II. These values follow:

Time (mins.)	1	5	15	30	60
x	0.046	0.134	0.200	0.241	0.345

The fact that x at the end of 60 minutes is 0.345 while $x_\alpha = 0.96$ is in itself sufficient evidence of the slowness of the decomposition of methane.

Equation 1 may be rearranged:

$$k_2 = \frac{1}{0.8686\,(x_\alpha + B)t} \cdot \log \frac{x + B}{x_\alpha - x} - \log \frac{B}{x_\alpha}$$

Table III gives the calculated values of k_2.

TABLE III

Time (mins.)	1	5	15	30	60
$k_2 \times 10^3$	1.7	0.96	0.52	0 32	0.32

Bone and Coward[3] emphasize the fact that an abnormal period occurs at the start of the reaction, this in their opinion being due to the reaction taking place at the walls of the reaction tube. After these have become coated with deposited carbon, the reaction proceeds to a greater degree normally. Table IV gives the values for $k_2 \times 10^3$ calculated with the fifth minute considered as the zero point.

TABLE IV

Time (mins.)	1	5	15	30	60
$k_2 \times 10^3$	—	—	0.24	0.16	0.15

The agreement is much better.

To complete the mathematical analysis, the graphical solution is added:

Let $Y = \log x + B/x_\alpha - x$

$b = \log B/x_\alpha$

$m = 0.8686\, k_2(x_\alpha + B)$

Then $Y = m\,t + b$

and if the values of Y as ordinates be plotted against the values of t as abscissae, the points will lie on a straight line. The most probable straight line may be drawn by determining two Average Points and connecting them. The slope of this line gives m; from which k_2 (the value of k_2 for the whole process) may be calculated.

Department of Chemistry,
University of Cincinnati,
Cincinnati,
Ohio.

---

[1] Ber., **40**, 2134 (1907).

[2] Cantelo: J. Phys. Chem., **28**, 1035 (1924).

[3] J. Chem. Soc., **93**, 1197 (1908).

THE ORIGIN OF THE CHARGE ON COLLOIDAL PARTICLES

BY HENRY BOWEN OAKLEY

Many investigators[1] have suggested that the charge of a colloidal particle may be due to the ionisation of the molecules on its surface. The fact that colloids of a basic nature usually carry a positive charge and those of an acidic nature a negative one is strongly suggestive of this view as has been pointed out by Noyes[2], Burton[3] and others.

According to the above idea the positive charge on a ferric hydroxide sol which contains a small quantity of hydrochloric acid, is due to the power of the molecules on the surface of the particle to dissociate into positively charged iron ions and negative chlorine and possibly hydroxyl ions. The iron ions are held to the particles because they form part of the complex molecular aggregate of ferric hydroxide. The chlorine ions, on the other hand are in true solution but, unless there are other negative ions distributed in the solution to replace them, they are unable to diffuse far from the surface of the particle because of the development of a strong electrostatic attraction by the positive ions on the surface.

In the same way the negative charge of a silicic acid sol containing a small quantity of sodium hydroxide may be regarded as being due to the ionisation of the surface layer of silicic acid and complex sodium silicate into hydrogen and sodium ions. The complex silicate ion remains on the surface of the particle because it forms a structural part of the large molecular aggregate. The sodium and hydrogen ions, although in true solution, are unable to diffuse away from the particle because of the electrostatic attraction of the negative ions on the surface.

Michaelis[4] has put forward a similar view to explain the charge and stability of mastic solutions and the swelling of agar gels. But it is Loeb[5] who has done most to develop this theory, and has applied it with remarkable success to the explanation in detail of the electrical and physical behavior of proteins.

Loeb showed that if this surface ionisation was a fact the distribution of ions between the surface layer and the bulk of the solution should be governed by the Donnan[6] equilibrium, and a potential difference between the particle and the solution should be the result of this equilibrium.

---

[1] J. A. Wilson: J. Am. Chem. Soc., **38,** 1892 (1916); J. A. and W. H. Wilson: **40,** 886 (1918).

[2] A. A. Noyes: J. Am. Chem. Soc., **27,** 85 (1905).

[3] Burton: "The Physical Properties of Colloidal Solutions", (1921).

[4] L. Michaelis: "Colloid-Symposium Monograph", **2,** (1925).

[5] Jacques Loeb: "Proteins and the Theory of Colloidal Behaviour".

[6] F. G. Donnan: Z. Elektrochem., **17,** 572 (1911); Donnan and Allmand: J. Chem. Soc., 105, 1963 (1914).

The Donnan Equilibrium

This equilibrium deals with the distribution of electrolytes on either side of a membrane. On one side of the membrane is an electrolyte one of whose ions is unable to diffuse through. All the other ions are diffusible.

The conditions satisfying the equilibrium for univalent ions may be briefly summarised as follows:—

Let z = concentration of non-diffusible negative ions.
then z = concentration of positive ions which are "partners" to the non-diffusible ions.
y = concentration of "free" positive ions on the same side of the membrane as the non-diffusible ions.
then y = concentration of the "free" negative ions on this side.
x = concentration of positive ions outside the membrane
then x = concentration of negative ions on this side.

Then on thermodynamic reasoning it can be shown that the product of the concentration of any two kinds of oppositely charged diffusible ions on one side of the membrane must always equal the product of the concentrations of the same two kinds of ions on the opposite side of the membrane.

$$\text{Hence } x^2 = y\ (y+z)$$

The membrane will be the seat of a potential difference between its two sides. By equating the electrical work done by moving one equivalent of ions across the membrane to the osmotic work done it may easily be shown that the potential difference is given by:—

$$\text{P.D.} = (RT/F) \log (y/x) = 0.058 \log y/x$$

y/x represents the ratio of the concentrations of the negative ions on the two sides of the membrane. If there are several kinds of negative ions, $a, b, c \ldots\ldots$ and a', b', c'.

$$\text{then } a/a' = b/b' = c/c' = (a+b+c)\ /\ (a'+b'+c')$$

Similarly if there are several kinds of positive ions
p, q, r and p', q', r'.

$$\text{then } p'/q = q'/q = r'/r = (p'+q'+r')/(p+q+r) = a/a'$$

Where the letters with a dash in both cases represent the concentration of the ions on the side of the membrane opposite to that of the non-diffusible ion.

In the first case the P.D. $= .058 \log a/a'$

and in the second case the P.D. $= .058 \log p'/p$

For a non-permeable acid the expressions a/a' or $p'/p \leq 1$ and the logarithm and P.D. will be negative.

For a non-permeable base the expressions a/a' or $p'/p \geq 1$ and the logarithm and P.D. will be positive, reckoned in both cases with respect to the side containing the freely diffusable substance only.

Application of the Donnan Equilibrium to Surface Ionisation

It will be realized from the foregoing that the important condition for the establishment of a Donnan equilibrium is that one kind of an ion shall be prevented from diffusing where all the others can so diffuse. This condition is fulfilled in the case of surface ionisation. Here the diffusion of one kind of ion is prevented, not by a membrane, but by its forming a structural part of a large molecular aggregate. The idea of a membrane is therefore to be replaced by the idea of a certain boundary near the surface of the particle beyond which the anions or cations, which are "partners" to the colloidal cations or anions as the case may be, are unable to diffuse because of electrostatic attraction.

It is not necessary to regard this boundary as being the position of a well-defined shell of ions, it is more natural to regard it as a "diffuse" boundary in which the ions are widely distributed about a mean position of equilibrium. The distance of this boundary from the surface must be regarded as being the average position at which the electrostatic attraction of the ions by the layer of non-diffusible ions just counterbalances the resultant osmotic pressure which tends to make the ions concentrated near the surface diffuse evenly throughout the solution.

Of course all the ions must be pictured in dynamic and not in static equilibrium.

Now let us apply this to a hypothetical case of a colloid acting as a weak acid, silicic acid for example:—

Four cases may profitably be considered.

(1) When the silicic acid contains no added electrolyte.

(2) When the only added electrolyte is a little hydrochloric acid.

(3) When the only added electrolyte is sodium hydroxide.

(4) When a neutral salt such as sodium chloride is also present in a neutral or alkaline solution.

Throughout what follows it will be assumed:—

(a) That the acid obeys the mass action law in dissociating[1].

(b) That the sodium salt is completely ionised.

(c) That neutral salts do not suppress the ionisation of the acid or its salt, and are themselves completely ionised.

Of course these assumptions can only be very roughly correct, but even wide deviations will not affect the general results in what follows.

(1) When there is no added electrolyte

Then if there is no silicic acid in true solution the aqueous phase will be neutral.

---

[1] The forthcoming mathematical treatment may, perhaps, lay undue stress on the importance of the validity of the dissociation equation to the theory. All that is really required for the argument is:—

(a) That the surface salts of a weak colloidal acid or base with a strong base or acid are much more highly ionised than the free acid or base.

(b) That these salts, owing to hydrolysis, are only formed in quantity when the solution in contact with them has a hydroxyl or hydrogen ion concentration above a certain minimum value depending on the strength of the acid or base. These conditions may still hold even if the dissociation equation is not valid.

Using the previous symbols:—

z = concentration of silicate ions bound to the surface of the particle.

then z = concentration of hydrogen ions which are partners to the silicate ions.

y = concentration of hydroxyl ions and also of the "free" hydrogen ions within the boundary.

x = concentration of the hydrogen and hydroxyl ions in the bulk of the liquid, and will be equal to 10-7 since this is neutral.

Also let C = maximum possible concentration of the silicate ions on the surface.

K_a = dissociation constant of silicic acid.

K_w = dissociation constant of water.

[By the concentration of the active molecules (or ions) on the surface of a particle is meant the effective concentration as equivalents per unit volume in the surface layer of the particle of the molecules (or ions) actively participating in the equilibrium. The thickness of this layer would have to correspond to the depth below the surface to which the equilibrium extended in any particular case. This concentration, as indeed all the concentrations, should really be expressed as an "activity" or thermodynamic concentration, but this will not affect the validity of the argument].

It can be shown that the concentration of the ions of a weak non-basic acid is

$$\frac{CK_a}{\sqrt{CK_a+K_w}}$$

When, as is usually the case CK_a is large compared with K_w this reduces to the well known expression, $\sqrt{CK_a}$, for the ionic concentration of a weak acid.

It has been shown recently by work in this laboratory[1] that the first acid constant of H_2SiO_3 is about 10^{-10}.

The value of C, the concentration of active silicic acid molecules on the surface of a particle is, of course, quite unknown. For the sake of argument suppose it is unity.

then $z = \sqrt{CK_a} = 10^{-5}$

y = OH-concentration $= K_w/Z = 10^{-9}$

$x = 10^{-7}$

and the surface P.D.[2] $= .058 \log y/x = .058 \log x/y+z = -.116$ volts

If $C = 0.01$ instead of unity:

then $z = 10^{-6}$ $y = 10^{-8}$ $x = 10^{-7}$ and P.D. $= -.058$ volts

---

[1] Joseph and Oakley: J. Chem. Soc., **127**, 2813 (1925).

[2] P. Ds. calculated in this paper are thermodynamic potential differences; these may not be identical with the "electrokinetic" potential differences, which are responsible for the migration of particles under an electric field. Which quantity may best be regarded as being the most important in preventing coagulation is quite unknown. Since the values set forth in this paper are not quantitative but only qualitatively illustrate relative differences found in practice even a rough parallelism between the two sorts of potential differences will be sufficient for the argument.

It will be noticed that the hydrogen ion concentration. $z+y$, near the surface of the particle is a hundred times and ten times respectively as great as that in the bulk of the solution.

This suggests a natural reason why such weakly acid substances such as clay or silica[1] can absorb the base and liberate the strong acid from such salts as sodium chloride.

There is much evidence that clay[2] is a weak acid, and the surface molecules of amphorous silica may be expected to become hydrated to form a complex silicic acid.

When sodium chloride is added to the water the sodium ions can replace the hydrogen ions from the surface of the clay or silica and these will now be free to disperse throughout the aqueous phase. The hydrogen ion concentration will be lowered near the surface and increased throughout the solution.

Since the hydrogen ion concentration near the surface is lowered it necessarily follows from the dissociation equation that the bound acid anions on the surface must increase.

This is brought about by the formation of the highly ionised sodium salt, equivalent in amount to the hydrogen ions liberated.

The above view also explains why silica or clay which has been treated with salt solution yields an alkaline solution on washing.

When the salt solution is replaced by pure water the sodium ions near the surface are replaced by hydrogen ions from the water, while the sodium ions diffuse into the aqueous phase and form sodium hydroxide. The action is that of hydrolysis taking place directly with the solid phase instead of through an intermediate solution phase.

(2) When the only added electrolyte is hydrochloric acid

then z = concentration of the silicate ions on the surface.

also z = concentration of hydrogen ions which are "partners" to these silicate ions.

y = sum of concentrations of the chlorine and hydroxyl ions within the boundary.

x = concentration of hydrogen ions and also the sum of the concentrations of chlorine and hydroxyl ions outside the boundary.

Then from the dissociation equation:—

$$z = CK_a/K_a + (H^{\cdot}) \text{ but } (H^{\cdot}) = y + z$$

$$\text{therefore } z = CK_a/K_a + y + z, \text{ also } x^2 = y\,(y+z)$$

Starting with assumed values of the hydrogen ion concentration within the boundary, x, y, and z can be calculated, assuming $K_a = 10^{-10}$, $C = 1$

This has been done in Table I:—

---

[1] A. F. Joseph and J. S. Hancock: J. Chem. Soc., **123**, 2022 (1923); **125**, 1894 (1924).

[2] R. Bradfield: J. Am. Chem. Soc., **45**, 2669 (1923).

TABLE I

Effect of Acid on the P.D. of a Negative Colloid.
x = hydrogen ion concentration.

$y+z$	z	y	$x=\sqrt{y^2+yz}$	P.D. = .058 log y/x volts
10^{-1}	10^{-9}	10^{-1}	10^{-1}	0
10^{-2}	10^{-8}	10^{-2}	10^{-2}	0
10^{-3}	10^{-7}	10^{-3}	10^{-3}	0
10^{-4}	10^{-6}	$.99 \times 10^{-4}$	$.995 \times 10^{-4}$	.0001

Table I shows that acids are very effective in suppressing the P.D. of a negative colloid. There is no need to postulate a specific absorption of hydrogen ions. The powerful effect of acids is merely the natural result of the suppression of ionisation of a weak acid by a strong one.

Bradfield[1] and Billiter[2] showed that silicic acid sol does not coagulate until a much higher concentration of acid or salt is reached than that required to abolish the surface P.D. Loeb[3] and Michaelis[4] quote other examples. Such substances have been designated by the terms lyophilic, hydrophilic or emulsoid colloids. It appears that these owe their stability to "solution forces" similar to those which hold a truly soluble substance in solution. On the other hand substances which are readily coagulated by small quantities of electrolytes have been designated by the adjectives lyophobic, hydrophobic or suspensoid, and these owe their stability to the existence of a P.D. at their surface. They coagulate when this P.D. is suppressed sufficiently, the more rapidly the greater the suppression.

Clay suspensions belong to this class. The table shows that a given suspensoid should be coagulated by different acids at those concentrations at which their hydrogen ion concentrations are the same. This has been proved for clay by Bradfield[5]. Exactly analogous reasoning can be applied to the effect of alkalies on positive colloids.

(3) When the only added electrolyte is sodium hydroxide

For the development of the theory we want to consider a negative colloid which does not go into true solution with sodium hydroxide.

This is not the case with silicic acid, which probably forms a system in which an equilibrium exists between colloidal aggregates of complex silicates and silicate molecules in true solution; the latter becoming the more predominant the greater the alkalinity of the solution.

Clay would appear to approximate more closely to the above conditions although even this is partially soluble in alkalies.

---

[1] "The Chemical Nature of a Colloid Clay". R. Bradfield: Bull. 60, University of Missouri, (1923).

[2] J. Billiter: Z. physik. Chem., **51**, 150 (1905).

[3] Jacques Loeb: "Proteins and the Theory of Colloidal Behaviour", (1921).

[4] L. Michaelis: "Colloid Symposium Monograph", **2**, (1925).

[5] R. Bradfield: J. Am. Chem. Soc., **45**, 1243 (1923).

For the sake of direct comparison with the two previous cases we will consider the behaviour of an ideal substance having the same values of K_a and C, and not passing into solution with alkalies.

Then z = concentration of the acid anions bound on the surface of the particle.
Also z = The sum of the concentrations of the sodium and hydrogen ions which are "partners" to these anions.
y = Sum of concentrations of the "free" sodium and hydrogen ions within the boundary.
Also y = Concentration of hydroxyl ions in the boundary.
x = The sum of the concentrations of the sodium and hydrogen ions outside the boundary.
Also x = Concentration of hydroxyl ions outside the boundary.

Then from the dissociation equation $z = CK_a/K_a + (H^{\cdot})$ but

$(H^{\cdot}) = K_w/y$ so that $z = CK_ay/K_ay + K_w$, also $x^2 = y\,(y+z)$.

Assuming different values of y, Table II can be constructed showing the corresponding values of z, x, and the surface P.D.

Table II

Effect of NaOH on the P.D. of Pure Negative Colloid.
x = OH-concentration.

y	z	x	P.D. $= .058 \log y/x$
10^{-7}	10^{-3}	10^{-5}	$-.116$
10^{-6}	9.9×10^{-3}	9.95×10^{-5}	$-.116$
10^{-5}	9.1×10^{-2}	9.54×10^{-4}	$-.115$
10^{-4}	0.5	7.07×10^{-3}	$-.107$
10^{-3}	0.91	3.02×10^{-2}	$-.086$
10^{-2}	0.99	0.10	$-.058$
10^{-1}	1.00	0.33	$-.030$
1	1.00	1.41	$-.009$

Table II shows that for small concentrations of alkali the P.D. remains constant and has the same value as for the colloid in pure water. Increasing concentrations of alkali gradually suppress the P.D. to nearly zero.

Table III shows the effect of having a smaller concentration of acid at the surface. C = .01 instead of 1.

Table III

y	z	x	P.D. volts
10^{-6}	9.9×10^{-5}	10^{-5}	.058
10^{-4}	5×10^{-3}	7.14×10^{-4}	.049
10^{-2}	9.9×10^{-3}	1.41×10^{-2}	.009
10^{-1}	1×10^{-2}	1.05×10^{-1}	.001

The same effect is observed except that the P. D. is less.

It should be remarked that the above results show, on the theory, that small quantities of alkali should not increase the P.D. of a negative sol and exactly similar reasoning may be applied to show that acids should not increase the P.D. of a positive sol.

This result is not in accordance with general experience. Thus Bradfield[1] found that the addition of sodium hydroxide to a clay sol increased the distance moved during twenty minutes in a cataphoresis experiment from 7.2 m.m. to 11.5 m.m., while further addition decreased the distance. Similarly ferric hydroxide has a greater migration velocity under an electric gradient in the presence of a small quantity of hydrochloric acid.

It will be shown, however, in the next section, that if there is a small quantity of neutral electrolyte present the theory predicts that the addition of alkali should at first greatly increase the P.D. and then depress it. Thus the observed results may be due to the presence of a small quantity of electrolyte.

It may be as well to emphasise the fact that the above result for the identity of the P.D. of the colloid in pure water with the value in the presence of alkali is only arrived at on the assumption that the surface acid (or base) of the colloid dissociates strictly according to the mass action law.

The fact that ferric hydroxide sol becomes unstable when very highly purified from hydrochloric acid may be taken to indicate, according to the views expressed in this paper that the ferric hydroxide itself does not undergo surface ionization to an appreciable extent, but that it is only a ferric hydroxide-chloride complex that ionises.

(4) When both sodium hydroxide and sodium chloride are present

It has been shown that the surface P.D. is proportional to the logarithm of the ratio of the concentration of an ion near the surface to the concentration of the same kind of ion in the bulk of the solution.

In a neutral or very slightly alkaline solution the concentration of the sodium ions near the surface of the particle is small. But their concentration in the neutral or slightly alkaline aqueous phase is so much smaller that the ratio of these two concentrations remains large. A very small addition of a neutral electrolyte will therefore be sufficient to equalize this ratio and abolish the P.D.

If alkali is now added the surface ionisation of the weak colloidal acid is immensly increased and a P.D. will again be established which will require a much greater addition of neutral electrolyte for its suppression.

This will be made clearer by working an example. In this case it is necessary to distinguish between the concentrations of the ions of sodium hydroxide and sodium chloride.

---

[1] "The Chemical Nature of a Colloidal Clay". R. Bradfield: Bull. 60, University of Missouri, (1923).

As before let z = Concentration of the anions bound to the surface of the particle.

Also z = Sum of concentrations of sodium and hydrogen ions which are "partners" to these anions.

y_1 = Concentration of hydroxyl ions within the boundary.

Also y_1 = Concentration of "free" sodium ions which are "partners" to these hydroxyl ions.

y_2 = Concentration of chlorine ions within the boundary.

Also y_2 = Concentration of "free" sodium ions which are "partners" to these chlorine ions.

x_1 = Concentration hydroxyl ions outside the boundary.

Also x_1 = Concentration of sodium ions which are "partners" to these hydroxyl ions.

x_2 = Concentration of chlorine ions outside the boundary.

Also x_2 = Concentration of sodium ions which are "partners" to these chlorine ions.

Then at equilibrium:—

$$(OH)_1\,(Na)_1 = (OH)_2\,(Na)_2$$
$$(Cl)_1\,(Na)_1 = (Cl)_2\,(Na)_2$$

Where the bracketed terms represent the concentration of the appropriate ion, and the suffixes 1 and 2 refer to opposite sides of the boundary.

Referring to the definitions we can write this as:—

$$x_1\,(x_1 + x_2) = y_1\,(y_1 + y_2 + z) \ldots\ldots\ldots\ldots 1.$$
$$x_2\,(x_1 + x_2) = y_2\,(y_1 + y_2 + z) \ldots\ldots\ldots\ldots 2.$$

As before $z = CK_ay_1/K_ay_1 + K_w \ldots\ldots\ldots\ldots 3.$

Dividing 2. by 1. we get $x_2/x_1 = y_2/y_1$ or $y_2 = y_1x_2/x_1 \ldots\ldots 4.$

Two special cases are of interest.

(a) To calculate the distribution of electrolytes and the P.D. when the concentration of the sodium chloride in the aqueous phase is kept constant but the alkali concentration is varied.

x_2 is kept constant; x_1 is varied at will. If y_2 is eliminated from equation 1. by substitution from 3. & 4. the result is a cubic equation in y_1 which is not easy to solve.

By solving for y_2 in 1. we get:—

$$y_2 = \frac{x_1(x_1 + x_2)}{y_1} - z - y_1 \ldots\ldots\ldots\ldots 5.$$

Equations 4. & 5. may conveniently be solved graphically.

For every value of x_1, (x_2 having an assumed constant value) two series of values of y_2 are calculated from 4. & 5. for different assumed values of y_1. These can be plotted against y_1 and the place where the curves cut gives the required values of y_1 and y_2.

Table IV shows in addition the pH values of the solution, calculated for tenth normal sodium chloride ($x_2 = 0.1$), and the previous values for K_a and C.

TABLE IV

Effect of NaOH on the P.D. of a Negative Colloid in the Presence of 0.1 N. NaCl. x_1 = OH-concentration

x_1	pH	z	y_1	y_2	y_1/x_1	P.D.
10^{-7}	7	0.001	10^{-7}	0.100	1.00	0
10^{-6}	8	.0094	9.5×10^{-7}	.095	.95	−.001
10^{-5}	9	.068	7.3×10^{-6}	.073	.73	−.008
10^{-4}	10	.256	3.45×10^{-5}	.033	.34	−.027
10^{-3}	11	.615	1.60×10^{-4}	.016	.16	−.046
10^{-2}	12	.909	1.20×10^{-3}	.012	.12	−.053
10^{-1}	13	.995	1.93×10^{-2}	.019	.19	−.041
1	14	1.00	6.45×10^{-1}	.060	.60	−.011

It will be seen that the sodium chloride is at first sufficient to suppress entirely the P.D. but that as the pH increases the P.D. rises to a maximum and then falls again.

With a stronger acid the position of this maximum would be at a lower pH value; it occurs when the alkali concentration near the surface is sufficient to convert nearly completely the weak acid into its ionised sodium salt.

The theory thus offers a natural explanation why alkalies are usually good deflocculants of negative colloids.

Precisely analogous results hold for the effect of acids on a positive colloid acting as a weak base.

The ratio of the hydrogen ion concentration in the bulk of the solution to that near the surface of the particle must also be equal to y_1/x_1; thus the hydrogen ion concentration near the surface of the particle is only equal to that in the bulk of the solution when this ratio is unity. That is to say when sufficient salt is present to suppress the P.D. to zero. Therefore in determining the strength of a colloidal acid such as clay by means of a pH-titration curve sufficient salt should be present to flocculate the clay.

Coagulation of Silicic Acid by Calcium Salts

Comber[1] has shown that silicic acid is very much more readily flocculated by calcium salts in an alkaline medium than in a neutral or slightly acid one.

Now calcium silicate is very insoluble, while the sodium silicates are very soluble.

The surface sodium silicate we have been considering may be regarded as being constructed of highly polar molecules. That is to say, while the acid groups and their attached sodium atoms (ions) have a very strong affinity for water, the silica groups forming the rest of the molecule have a much stronger affinity for each other than for the water. The result is a compromise, a colloidal solution.

---

[1] N. M. Comber: J. Agr. Sci., **19**, 425 (1920).

On the other hand the calcium silicates have practically no affinity for water in this sense, as is shown by their insolubility. Thus the complex calcium silicate aggregates will show little or no tendency to surface ionisation.

Since silicic acid is very weak its salt will not be formed to any extent until the solution is alkaline. Directly the alkalinity is such that surface calcium silicates can be formed, these will be unionized and the silicic acid and silicates will be precipitated. The fact that neutral salts only coagulate silicic acid at high concentrations is to be ascribed to its lyophilic nature, as mentioned when discussing the effect of acids.

(b) The second case of interest is to assume a certain constant low value of the P.D. and to calculate the amount of sodium chloride required to depress it to this value for different concentrations of alkali.

Let the P.D. be kept constant at $-.058/10$ volts.

Then $\log y_1/x_1 = -1.0 = \bar{1}.9$ whence $y_1 = 0.7943\ x_1$ and since $y_1/x_1 = y_2/x_2$ therefore $y_2 = 0.7943\ x_2$..............................6.

Then substituting equation 6. in equation 1. and solving for x_2 we obtain:—

$$x_2 = (y^2_1 + y_1z - x^2_1)/(x_1 - .7943y_1) \text{ where } z \text{ is given by } 3.$$

Then by assuming values for x_1 all the other quantities may be calculated as in Table V.

TABLE V

$K_a = 10^{-10}$ P.D. = .0058 volts C = 1

The minimum sodium ion concentration required for the coagulation of a negative colloid at different pH values.

Na-ion concentration = $x_1 + x_2$

x_1	pH	y_1	z	x_2	y_2	x_1+x_2
10^{-7}	7	7.94×10^{-8}	.0008	.002	.0017	.0021
10^{-6}	8	” 10^{-7}	.0078	.017	.0135	.017
10^{-5}	9	” 10^{-6}	.073	.158	.125	.158
10^{-4}	10	” 10^{-5}	.443	.953	.76	.953
10^{-3}	11	” 10^{-4}	.889	1.91	1.52	1.91
10^{-2}	12	” 10^{-3}	.988	2.1	1.67	2.11
10^{-1}	13	” 10^{-2}	.999	2.05	1.27	2.15
1	14	” 10^{-1}	1.000	1.15	0.90	2.15

The last column of Table V shows the total sodium ion concentration in the bulk of the solution, while the second column shows the pH of this solution. If this particular colloid just became unstable when the P.D. of its particles was reduced to .006 volts, then the last column would represent the minimum concentration of sodium ions required to produce coagulation.

If this quantity is plotted against the pH it will be found that it increases slowly from a pH of 7 to 9. This is followed by a very rapid rise between a pH of 9 to 11 and reaches a constant value between a pH of 11 to 14.

This is precisely the type of result obtained by Bradfield[11] for the minimum potassium ion concentration required for the coagulation of a clay suspension at different pH values. At high pH values it was immaterial whether the base or its salt was used as the coagulating electrolyte. In Bradfield's experiment the sudden increase in electrolyte requirement took place between pH values of 6 and 8; this indicates, on the theory, that the dissociation constant of the clay acid is in the neighborhood of 10^{-7}.

The foregoing results have shown that the theory offers a natural explanation for the more characterisitc behaviour of colloids towards acids, alkalies and salts of the alkali metals.

The effect of the valency of the ion has not been considered. Loeb showed that the Donnan equilibrium predicts that the ions of higher valency should be more effective in depressing the P.D. The ratio of the P.Ds. for uni-valent, di-valent and tri-valent ions at the same concentration and pH should be in the ratio of 2; 3; 4. Loeb showed this held for uni-valent and di-valent ions with proteins. Usually the precipitating power of polyvalent ions is too great to be accounted for solely on these lines. The high precipitating power may be accounted for on the hypothesis that the surface ionisation of their compounds is much less than that of the corresponding alkali metal compound. Much of the data has, however, been obtained without control of the hydrogen ion concentration.

Many exceptions may be found to the behaviour of colloids outlined in this paper, but these are not necessarily irreconcilable with the notion of surface ionisation. Sols which can be made either positive or negative will usually be found to be of a slightly amphoteric nature, e.g. ferric hydroxide and chromium hydroxide. That is to say under suitable conditions they can be made to ionise as an acid or as a base. Metallic sols presumably form some surface compound with water or with electrolytes present during their preparation. Thus gold sol may be negative because of the surface ionisation of an auric acid complex[1]. Other metallic sols may owe their positive charge to the ionisation of a surface layer of hydroxide.[2] The sign of metallic sols may be changed by polyvalent ions because of the formation of a surface "salt" of this ion with one of its valencies, while its other valencies are free to ionise.

The peculiar base exchanging properties of zeolites, clay and artificial alumino-silicates may be attributed to the surface ionisation of the compounds of these substances with bases. The fact that calcium is held more tenaciously than sodium is in agreement with the idea that the calcium compounds are much less ionised that the sodium compounds, as has been suggested for silicic acid.

Adopting Loeb's theory as an hypothesis will at any rate serve as a guide in the making of experiments and will afford a strong reason for the control of the pH in all investigations on colloids. Its success in accounting for the behaviour of clay and proteins towards electrolytes is strong evidence for the truth of its assumptions[3].

---

[1] J. A. Wilson: Bogue's "The Theory and Application of Colloidal Behaviour", **1**, (1924).

[2] Burton: "The Physical Properties of Colloidal Solutions" (1921).

[3] For application of the theory to living cell boundaries see:—Lapicque: Ann. de Physiologie et de Physicochimie biologique, **1**, No. 1; Nature, **116**, 150 (1925).

The Nature of the Electrical Double Layer

In the whole of the foregoing the assumption has been made that the force on a particle during cataphoresis and its stability are proportional to the potential difference existing at its surface, and not to the charge on the particle.

This is an essential part of the theory. Thus a pure clay suspension at a low pH may cataphorese as rapidly as it does in an alkaline medium[1], although, if the clay is behaving as a weak acid, the ionisation and therefore the charge must be immensely greater in the latter case. Hitherto the assumption has always been made by writers that the force on a charged particle is always equal to the product of its charge and the potential gradient in the solution, in spite of its being recognised that the particle as a whole acts as an electrically neutral condenser whose outer charge is mobile.

This is surely a fallacy. The law F = QV, where F = force, Q = charge, V = potential gradient, only applies to a charge whose potential is not modified by any other charges in its neighbourhood, even if these charges are mobile.

A truer statement is to say that the shearing force between a particle and the surrounding liquid is proportional to:—

(a) The potential gradient in the liquid.

(b) The P.D. between the particle and the liquid.

(c) The area over which this P.D. exists.

This will lead to the result that particles of the same kind but of different diameters will still have the same cataphoresis velocity. This is the result arrived at by the old assumption that the force is proportional to the charge.

Early in this paper, for the purpose of applying the Donnan equilibrium, the position of the boundary was defined as the average distance from the surface taken up by the ions as the result of a balance between the osmotic and electrostatic forces. This boundary may also be considered as the position of the outer electrical layer. The inner layer is formed by the bound ions on the surface of the particle.

We will consider the behaviour of this double layer under two conditions:—

(a) When the P.D. remains constant but the ionisation, and therefore the charge on the two layers is increased. This corresponds to the conditions dealt with in section (3), when small quantities of sodium hydroxide are added to the pure colloid.

Since the charge on the two oppositely charged layers is greatly increased, the only way for the P.D. to remain constant is for the distance between them to decrease. This at first sight may seem strange as the repelling force due to osmotic pressure is also greatly increased, but it will be shown that the attractive electrical force increases to a much greater extent.

The resultant osmotic pressure tending to make the ions within the boundary diffuse throughout the solution is proportional to the difference in the total ionic concentrations on the two sides of the boundary.

Assuming the osmotic pressure due to the anions bound on the surface is negligable, the resultant pressure is proportional to $z + 2y - 2x$.

Referring to Table II:—

y	$z + 2y - 2x$
10^{-7}	9.8×10^{-4}
10^{-5}	9.7×10^{-2}

In changing the OH-concentration, y, from 10^{-7} to 10^{-5} there is a hundred-fold increase in the resultant osmotic pressure on the outer layer, tending to drive it further away from the surface of the particle.

The electrostatic attraction between the two layers is, however, proportional to the *square* of the charge on either layer i.e. it is proportional to z^2.

Hence for the same example:—

y	z^2
10^{-7}	10^{-6}
10^{-5}	8.3×10^{-3}

Thus there is an eight thousandfold increase in the attractive force.

The two electrical layers will therefore be closer together the greater their charge, and by this means the P.D. can remain constant.

(b) When the ionisation and therefore the charge on the two layers remains constant, but the P.D. is diminished.

These conditions correspond to a case in which the OH-concentration near the surface of the particle is by some means kept constant while the P.D. is diminished by the addition of a neutral electrolyte.

In this case the electrostatic attractive force remains constant but the *resultant* repulsive osmotic force is decreased by the neutral electrolyte. (When the P.D. is completely suppressed there is no resultant osmotic force.) The two electrical layers therefore approach very close together and by this means depress or eliminate the P.D. between them.

Since existing formulae for the charge and P.D. of particles based on data from cataphoresis or endosmosis experiments are, on this view untenable, it becomes desirable to look for other means of measuring these quantities.

When colloidal particles are charged and also move under an electric field (the two terms are not necessarily synonimous, as shown above) they must always possess an electrical conductance of their own.

This conductance must be regarded as being made up of two parts:—

(a) The conductance due to the electricity carried by the particle itself i.e. the charge on the inner electrical layer.

(b) The conductance due to the electricity carried by the ions forming the outer electrical layer. This charge is equal and opposite to that on the surface itself, and moves in a direction opposite to that of the particle. As fast as these ions leave the particle they are replaced by other ions from the solution.

The specific conductance of any substance is equal to the quantity of electricity conveyed per second through unit cross section of the substance under unit potential gradient. Therefore in cataphoresis experiment with unit potential gradient

If k = specific conductance due to the colloid alone in 1 c.c. of the solution.
V_1 = velocity of the particles themselves.
V_2 = velocity of the outer layer of ions relative to the electrodes.
Q faradays = charge of one sign carried by one particle.
n = number of particles in 1 cc. of the solution.
F = number of colombs in one faraday.
Then $k = nF\ (QV_1 + QV_2)$

Now if we suppose the force on the particle is also equal to the force on its outer layer, that is to say if we suppose the two forces are related as action and reaction, then the force on one ion of the outer layer will equal $1/Q$ of the force on the particle. Let us also assume that the velocity of a particle or ion is proportional to the force acting on it, as in Stokes' law.

Then if f_1 = force on the particle.
f_2 = force on one ion in the outer layer.
$V_1 = K_1 f_1$ and $V_2 = K_2 f_2$, where K_1 and K_2 are constants.
but $f_2 = f_1/Q$ and $f_1 = V_1/K_1$
therefore $V_2 = K_2 V_1/K_1 Q$ and $k = nF\ (QV_1 + K_2 V_1/K_1)$

From which the charge in coulombs carried by the particles in 1 c.c. of solution is given by:—

$$FnQ = (k/V_1) - nF\ (K_2/K_1)$$

The ratio K_2/K_1 represents the ratio of the velocity of an ion to that of the particle itself when both are subjected to the same driving force. Its value is therefore quite unknown.

V_1 can be measured from a cataphoresis experiment.

k, the conductance due to the colloid alone might be obtained by measuring the conductance of the colloidal solution before and after careful filtration through an ultra filter of sufficient fineness to retain the colloidal particles. The difference would give the conductance due to the colloid alone. Then the ratio, k/V_1 would be proportional to the charge on the colloid. Its variation in the presence of electrolytes, specially alkalies, should help to test the theory.

Summary

1. The theory of surface ionisation has been developed to explain the charge on colloids.

2. By combining the equation for the Donnan ionic equilibrium with that for the dissociation of weak acids or bases, Loebs views have been developed to give a rational explanation of the general behaviour of colloids towards acids, bases and salts.

3. It has been pointed out that R. Bradfield's work on the behaviour of clay suspensions agrees closely with that predicted by the theory.

4. Rational deductions from the theory have been made as to the nature of the electrical double layer of colloids.

5. The present method of measuring the charge on colloids is adversely criticized and an alternative is suggested.

Wellcome Tropical Research Laboratories,
Khartoum,
Jan. 20, 1926.

AQUEOUS SOLUTIONS OF SODIUM SILICATES. PART III. SODIUM ION ACTIVITY

BY R. W. HARMAN

Introductory

The problem of the nature of the ions and their respective concentrations in aqueous solutions of sodium solicates cannot be determined solely by measurements of the total number of ions, say by means of vapour pressure or freezing point measurements and by measurement of the extent of the hydrolysis of these solutions. The number of ions deduced, assuming the laws of ideal solution to apply, from freezing point measurements (as will be seen from the discussion of those measurements in a paper to be communicated soon) is not in agreement with that which would correspond to the percentage hydrolysis if hydrolysis only took place. Hitherto, the silica in solution derived from the dissociation of silicate solutions has been considered colloidal, and the suggestion has been put forward that complete hydrolysis takes place, the low value found for the degree of hydrolysis being only apparent, since such degree of hydrolysis has been computed from the 'free' hydroxyl ion concentration (as measured by the hydrogen electrode), whereas the silica may be colloidal and may adsorb hydroxyl ions. If such were the case, then the hydroxyl ion concentration plus the sodium ion concentration should equal the total ion concentration as found by freezing point measurements. However, both conductivity and transport number experiments[1] give evidence of silicate ions or complex ionic aggregates being present in solution. If this is so, and the sodium ions are equivalent to the sum of the silicate and hydroxyl ions, and the sum of these three ions is equal to the total ion concentration, then correct conclusions can be drawn as to what really takes place in solution, the extent of both hydrolytic and ionic dissociation can be determined, and the question of the existence of colloidal or crystalloidal silica may be definitely settled. Hence the importance of determining the concentration of either the sodium or the silicate ions.

The concentration of the silicate ions is not capable of direct measurement, although a colorimetric method is useful whereby the amount of crystalloidal silica in solution may be deduced in very dilute solution. Experiments relating to the concentration and diffusion of the silicate ions are in progress and will be communicated in a later paper.

The sodium ion activity can be measured directly by means of the sodium amalgam electrode devised by G. N. Lewis, and from this we can get a fair conception of the sodium ion concentration, in fact, a correct measure of the concentration in very dilute solution; and if the assumption be made that the laws of ideal solution apply, as is usually done with the hydrogen electrode, i. e. that the ion activity gives a measure of the ion concentration, we can determine the sodium ion concentration in the more concentrated solutions.

---

[1] "Aqueous Solutions of Sodium Silicate," Parts I and II: J. Phys. Chem., 29, 1155 (1925); 30, 359 (1926).

Experimental

The technique of measurements with the alkali amalgam electrode first used by Lewis and Kraus[1] has since been developed and perfected by Lewis and by MacInnes and their co-workers, until now, the E. M. F. between a sodium amalgam electrode and a solution containing sodium ions is capable of very accurate and reproducible measurement, providing care is taken with the preparation of the amalgam, with the preparation of the solution to be experimented upon, and with the design and operation of the cell.

Preparation of Amalgam:—The mercury was purified according to Hulett's method by running it several times in a very fine spiral spray through 5% mercurous nitrate solution acidified with HNO_3, and then twice distilling it in a current of air at a pressure of 25 mm., the resulting scum of oxides (very little in the second case) being separated by filtration. The sodium amalgam was prepared in vacuo by a method similar to that employed by MacInnes and Parker.[2] As pointed out by these authors, the method is quite simple and very convenient but care must be taken in melting the sodium, as the capillary on the side tube through which the molten metal filters from the oxide is apt to become blocked and may cause an explosion.

The Amalgam Electrode:—The cell used was somewhat similar in design to that used by Lewis and Kraus.[1] It was found necessary to have the platinum contact with the amalgam sealed in the capillary tube without distorting the capillary and to have the platinum bent down into the capillary about 5 mm. to prevent the amalgam thread breaking when it was allowed to run out during an experiment.

The electrode vessel was filled by sealing it to the amalgam preparation vessel, evacuating with the vacuum pump and then allowing the amalgam to run down into the electrode vessel. The amalgam preparation vessel was then replaced by a P_2O_5 tube. By this means dry air, which has no effect on the amalgam, replaces the amalgam as it is used during the course of an experiment.

Design and Operation of the Cell:—Two side reactions interfere with the complete reversibility of these amalgam electrodes, but both have been eliminated. The two difficulties are:—

(1) the side reaction

$$2\,Na + 2H_2O = 2NaOH + H_2.$$

This causes decrease of potential difference between electrode and solution owing to the concentration of the amalgam being lowered, and the ion concentration in its vicinity being increased.

---

[1] J. Am. Chem. Soc., **32**, 1459 (1910).

[2] J. Am. Chem. Soc., **37**, 1445 (1915).

[1] J. Am. Chem. Scc., **32**, 1459 (1910).

The cell was designed so that, as the sodium amalgam flowed out of the capillary, it dropped through the silicate solution and out of contact with it, by passing through a tap through which, of course, some silicate solution also passed. In this manner fresh silicate solution is always continually passing the fresh amalgam surface. By this means very reproducible results were obtained, the P. D. remaining constant to within 0.1 millivolt for 20-30 readings.

(2) the side reaction:—

$$4Na + O_2 = 2Na_2O.$$
$$Na_2O + H_2O = 2NaOH.$$

due to dissolved oxygen in the solution. This also lowers the P. D. This difficulty was eliminated by preparing the solutions free from oxygen in the following way. A 300 to 400 cc. portion of concentrated solution of the desired ratio, made up from freshly distilled air-free water, had pure nitrogen bubbled through it for a couple of hours, and was then left in a flask tightly stoppered with a cork carrying an inlet and an outlet tube. This stock solution was accurately analysed and hence its concentration found. From this stock solution more dilute solutions were prepared by forcing a little of it out into a weighed flask by applying a pressure of nitrogen, weighing, and then adding freshly distilled water, prepared air-free by the same means, and weighing again. Any air in the flask above the solution was replaced by nitrogen. The solution so prepared was allowed to stand overnight, and when required for use in an experiment the requisite amount was driven over into the electrode vessel by applying a pressure of nitrogen.

Connection was made with the normal calomel electrode used to complete the cell by having some of the same silicate solution that was being investigated in a connecting tube dipping into a small beaker of the same silicate solution. The side limb of the calomel cell also dipped into this beaker.

The normal calomel electrodes used were very carefully made up from purified materials and they agreed with one another and with other calomel electrodes made up by different investigators in this laboratory to within 0.1 millivolt. The tap on the side limb of the calomel cell was kept closed during a measurement but some KCl was run out through this limb just before and after any series of measurements were made.

The whole apparatus was kept in an air thermostat electrically heated and regulated to 25°C ±0.01.

The measurements were made on a Cambridge and Paul potentiometer with two standardised Weston cells in series balanced against two accumulators, so that the readings in volts on the scale had merely to be doubled to get the observed E. M. F.

Concentration of Amalgam:—A weighed quantity, about 20 gms., of the sodium amalgam was run out of the electrode vessel into a porcelain dish and was left overnight, with occasional stirring by means of a platinum wire, in contact with a considerable excess of standard HCl. When complete decomposition had taken place the remaining HCl was titrated with NaOH. Two quantities of amalgam were prepared at different times, and both were analysed twice, once when the electrode vessel was nearly full and once when nearly empty. The concentration of the amalgam was found to be,—

1. 0.06057.
   0.06055%
2. 0.07090
   0.07091%

Calculation of Results

If we know the electrode potential between a sodium amalgam electrode and a solution of known sodium ion activity then it is easy to calculate the sodium ion activity of any other solution containing sodium ions, from the E. M. F. observed with the same sodium amalgam electrode in this particular solution. So measurements were first made of the E. M. F. due to the sodium amalgam in a standard solution of NaOH, i. e. of the following combination,—

$$(1) \quad \text{Na amal.} \mid \text{NaOH} \mid \text{N.KCl. } Hg_2Cl_2 \mid \text{Hg.}$$

and then the following was investigated,—

$$(2) \quad \text{Na amal.} \mid \text{Na sil.} \mid \text{N.KCl. } Hg_2Cl_2 \mid \text{Hg.}$$

varying the concentration and ratio of the sodium silicate in (2).

Now,—

$$(1) \quad E_{\text{amal.} \mid \text{NaOH}} = E_0 - RT/nF \ln a_{Na} \text{ (in NaOH)}$$

$$(2) \quad E_{\text{amal.} \mid \text{Na sil.}} = E_0 - RT/nF \ln a_{Na} \text{ (in Na sil.)}$$

Hence,

$$E_{\text{amal.} \mid \text{Na sil.}} - E_{\text{amal.} \mid \text{NaOH}} = RT/nF \ln \frac{a_{Na} \text{ (in Na sil)}}{a_{Na} \text{ (in NaOH}}$$

The concentration of the first preparation of sodium amalgam was 0.06056%, and the E. M. F. observed between this amalgam and a 1.0N.NaOH, corrected for the liquid potential difference 1.0 N.NaOH | 1N.KCl, calculated by means of the Henderson formula, was 2.1035 volts. The activity coefficient[1] γ of 1.0 N.NaOH was taken as 0.75 whence $a_{Na} = 0.75$. This $\gamma(=0.75)$ is the mean activity coefficient of the ions; so, to get the activity of the sodium ion the assumption is made that the sodium and hydroxyl ion coefficients are equal. Hence, for the series of measurements made with the sodium amalgam whose concentration was 0.06056% we get the working formula,

$$E_{\text{amal.} \mid \text{Na sil.}} - 2.1035 = 0.5911 \text{ Log } a_{Na}/0.75.$$

For the second preparation of amalgam used in the latter part of the measurements, the concentration of the amalgam was 0.0709%, the NaOH was 0.6708N, whence a_{Na} in NaOH = 0.5031, and the E. M. F. (corrected for liquid potential difference) was found to be 2.1142 volts.

---

[1] See Harned: J. Am. Chem. Soc., 47, 676 (1925).

Values for a_{Na} for the same silicate solution, obtained by the amalgams of the first and second preparations, agreed within 0.1%.

Liquid-Liquid Potential Difference:—The values of E. M. F. given in Tables I-II have been corrected for the P. D. between the sodium silicate solution used and N.KCl, by making use of the P. D. found between these silicate solutions and saturated KCl by the Bjerrum extrapolation method, and of the P. D. between saturated KCl and N.KCl calculated by means of the Henderson formula.

Results

Table I

N_w	E. M. F.	A_{Na}	$\gamma = a_{Na}/N^w$
Ratio 1 :			
0.832	2.1196	0.4006	0.481
0.373	2.1436	0.1573	0.422
0.111	2.1750	0.04629	0.417
0.043	2.1956	0.02166	0.504
0.020	2.2042	0.01485	0.739
0.00823	2.2200	0.008021	0.974
Ratio 1 : 2			
0.8486	2.1330	0.2331	0.275
0.5408	2.1428	0.1623	0 300
0.2056	2.1596	0.08433	0.410
0.084222	2.1788	0.03992	0.474
0.0403	2.1960	0.02043	0.507
0.02296	2.2090	0.01233	0.537
0.01349	2.2160	0.009374	0.695
0.002519	2.2500	0.002493	0 980
Ratio 1 : 3			
1.073	2.1520	0.1122	0.105
0.3829	2.1604	0.08175	0.213
0.1142	2.1788	0.04062	0.356
0.05454	2.1942	0.02239	0.411
0.01671	2.2150	0.009917	0.594
0.006594	2.2320	0.005135	0.779
Ratio 1 : 4			
0.7039	2.1766	0.04426	0.063
0.3215	2.1770	0.04358	0.135
0.09517	2.1916	0.02468	0.259
0.04479	2.2080	0.01582	0.353
0.01685	2.2220	0.007492	0.445

TABLE II

γ(Activity Coefficient) for Ratios

Conc. (N_w)	1 : 1	1 : 2	1 : 3	1 : 4
1.0	—	0.265	0.105	0.050
0.80	0.475	0.275	0.145	0.060
0.50	0.440	0.310	0.185	0.090
0.40	0.425	0.335	0.210	0.110
0.20	0.415	0.410	0.295	0.185
0.10	0.425	0.460	0.365	0.250
0.05	0.500	0.500	0.425	0.325
0.025	0.700	0.525	0.480	0.405
0.01	0.975	0.850	0.700	0.550

These results are shown graphically in Fig. 1, where γ is plotted against the concentration.

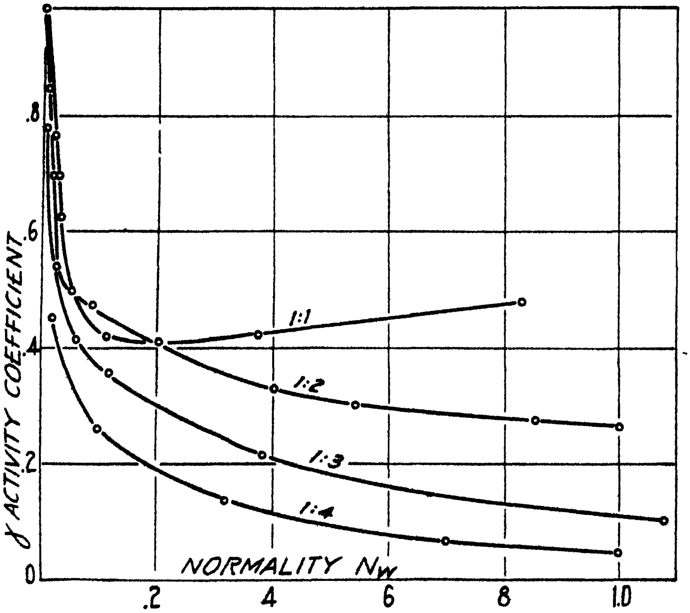


FIG. 1
Sodium Ion Activity γ against Concentration

Discussion of Results

The values for γ, the activity coefficient of Na_2SiO_3 (i. e. ratio 1:1) show that in concentrated solution as much as 40% of the total sodium exists in the active ionic state, while in dilute solution practically all the sodium exists so. The most remarkable feature is that γ for ratio 1:1 passes through a minimum at concentration $0.2N_w$, while none of the other ratios exhibit such a minimum. It is not unusual to find this minimum in γ for strong electrolytes in concentrated solution, and this has been shown by Debye and Hückel[1] to have a theoretical basis when the inter-ionic forces are taken into account.

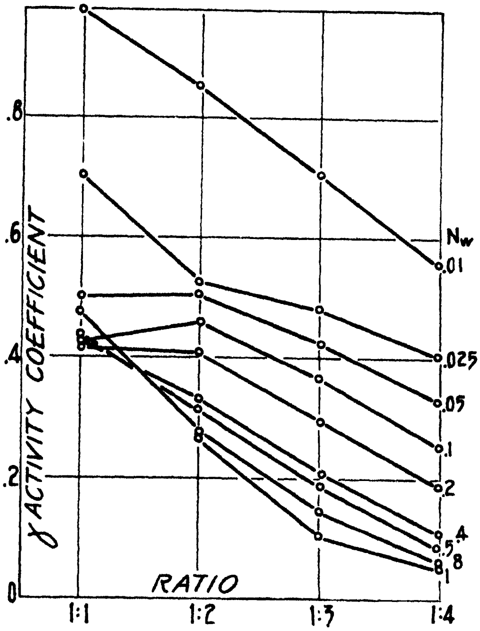


Fig. 2
γ against Ratio

In ratio 1:3 and 1:4, the values of γ are very low in concentrated solution and even in dilute solution are still comparatively low, indicating that all the sodium in solution does not exist as sodium ion, or if so, the silica present has considerably affected and reduced its activity.

When γ is plotted against the ratio, as in figure 2, then for $0.1N_w$ solution, the decrease in γ is quite regular as the proportion of SiO_2 increases.

The decrease in γ is also regular for the higher concentrations beyond ratio 1:2, but owing to the fact that γ for 1:1 passes through a minimum, and is even lower than γ for 1:2 at concentrations near $0.1-0.2N_w$, the changes of direction in the curves above 1:1 are varied and probably have no special significance.

---

[1] Physik. Z., **24**, 185, 334 (1923).

The general conclusion may be drawn however, that both increase of concentration for any given ratio, and increase of ratio for any given concentration, have a very marked effect on the activity of the sodium ion, so reducing it, that in concentrated solutions of ratios 1:3 and 1:4 it is remarkably low.

Summary

(1) Measurements of sodium ion activity by means of a sodium amalgam electrode have been made for ratios 1:1, 1:2, 1:3, and 1:4, at concentrations ranging from 1.0-0.01N.

(2) The activity coefficient γ has been plotted against the weight normality, N_w, and against the ratio $Na_2:SiO_2$.

(3) The curve of γ against N_w for ratio 1:1 passes through a minimum at a concentration lying between $0.1-0.2N_w$. The other curves show no minimum.

(4) In very dilute solution γ is high, but not so high as in corresponding concentrations of NaOH, whereas in concentrated solutions of higher ratios γ is abnormally low.

I wish to thank the Commissioners of the 1851 Exhibition for a research scholarship which has enabled me to carry out this work, and to express my gratitude to Prof. Donnan at whose suggestion this investigation was undertaken, for his constant kindly interest and advice.

The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College,
London,
April 7, 1926.

THE ELECTRODEPOSITION OF RADIUM D AND RADIUM E

BY JOHN P. McHUTCHISON

As the result of much investigation mainly by Hevesy and his co-workers, the chemical identity of the radio-elements with their isotopes, both amongst the ordinary elements and also amongst the radio-elements themselves, has been found to extend to their electrochemical behaviour.[1] In another series of experiments von Hevesy[2] proved that electrodeposition of radio-elements is possible when the E. M. F. employed is lower than the decomposition potential of their ordinary isotopes, and that "every metal is capable of causing the deposition of every radio-active body to a greater or less degree." He emphasized the fact that the main consideration is not the voltage nor the current density, but the potential of the electrode. The single electrode potential method had been previously employed by von Lerch,[3] who obtained deposits of radio-elements by dipping metallic plates in salt solutions containing radioactive matter. The extension of this last principle by von Hevesy established the most important fact that the ratio of the B- to the C-members of a radioactive series deposited on a metal plate depended on the E. M. F. Metal | Solution. He found that when the definite potential of a metal is +0.5 or greater (measured against the calomel electrode) a certain ratio is very high, and that this ratio diminishes as the potential becomes more negative, being about 7 for 0.0 volt. about 1 for −0.6 volt, and about 0.2 for −2.0 volts. The ratio referred to is the quantity of the isotope of bismuth to that of the isotope of lead deposited on a plate dipped into a solution containing these isotopes in radioactive equilibrium.

The present set of experiments is concerned with the deposition of the radio-elements, radium D and radium E, on metallic plates in neutral aqueous solutions, that is for the case of the indefinite E. M. F. Metal | Water. Such indefinite E. M. F.'s were included by Hevesy in his generalisation that every metal is capable of causing the deposition of every radioactive body: and the same investigator also measured the indefinite E. M. F. Copper | Water, and found it 0.7 volt more negative than the definite E. M. F. Copper | N-Copper sulphate, and from the present extension of von Hevesy's work, this last result appears to be of general application.

I.

Metallic Deposition of Radium D and Radium E in Pure Aqueous Solution

The active solution dealt with contained radium D, radium E, and radium F in radioactive equilibrium, and was obtained by dissolving in pure concentrated nitric acid the active deposit as formed on old radon tubes. The acid extract was evaporated to dryness in a platinum basin, and the active matter dissolved off in distilled water of conductivity standard. Thus a solution was obtained of these radio-elements as nitrates in pure water. The electroscopic measurements were performed with a beta-ray electroscope through one thickness of gold-beater's skin and two centimetres of air, so as to cut off all the alpha-radiation from radium F. The experiments described, therefore, are concerned only with radium D and radium E.

---

[1] Paneth and von Hevesy: Monatsheft, **34**, 1593, 1605 (1913); Wien. Ber., **123**, 1909 (1914).

[2] Von Hevesy: Phil. Mag., (6) **23**, 628 (1912); **25**, 390 (1913).

[3] Ann. Physik, (4) **12**, 766 (1903); Jahrb. Radioakt., **1905** II, 471.

Plates of the metals shown in Fig. 1, as pure as could be obtained, were immersed in quantities of the active solution for one hour at room temperature, and therefore, (except in the case of magnesium), for one hour or more at boiling point. When the solutions had cooled, the plates were removed, washed free of adhering solution by being dipped twice in pure water and once in alcohol. Measurements of the activity of the deposits on the plates were made regularly, and the results are shown in Table I.

Activities are expressed in arbitrary units, namely divisions of electroscope scale per minute. A quantity of active solution equal to that used in each case was evaporated to dryness, and gave an activity of 165.

TABLE I

Metal.	Initial Activity	Activity after 4.9 days	Percentage of radium D extracted.	Percentage of radium E extracted.	Remarks
(I)					
Magnesium	46	46	28%	28%	Magnesium acted on by water.
Aluminium	51	26	0%	100%	Almost pure radium E extracted.
Zinc	95	130	100%	58%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=1.7$
Nickel	68	34.5	0%	100%	Almost pure radium E extracted.
Tin	37	25	8%	20%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.4$
(II)					
Lead	60	50	24%	36%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.6$
(III)					
Copper	66	44	13%	43%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.3$
Silver	14	9	2.5%	8.5%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.3$
Platinum	27	15	2%	16%	$\frac{\%\text{ D extracted}}{\%\text{ E extracted}}=0.1$

The metals in *(I)* are more electropositive than lead or bismuth, the isotopes of radium D and radium E, while those in *(III)* are more electronegative.

The period of radium E is taken as 4.9 days (c. f. part 2 of this paper.)

Parallel experiments gave very similar results, and experiments involving immersion of the plates for twenty-four hours or longer were unsuccessful in extracting appreciably greater quantities of the active matter.

In Table I, the deposits obtained on the various metals are greatly different. First, whereas the rest of the metals extract radium D and radium E in other than their equilibrium proportions, magnesium extracts about 3/10ths of the equilibrium quantity of each, possibly an anomalous effect caused by the chemical action of the water on the plate. Second, the deposit on a zinc plate contained radium D in excess of its equilibrium quantity of radium E. The activity on an iron plate, which was also tested, was practically nil, since rust was formed and all the activity was adsorbed by it. It is worthy of notice that both aluminium and nickel extracted practically radium E alone, and use has been made of this to redetermine the half-life period of radium E. In the case of the more electronegative metals, it is clear that the ratio of radium D to radium E extracted becomes smaller with increase in electronegativeness, which was also the result obtained by Hevesy in 1912 for definite potentials.

Another observation made by von Hevesy for definite potentials is also proved by the above results to hold for indefinite potentials: namely, that the more electropositive metals replace the active isotopes of lead and bismuth in quite an anomalous way to what might be expected from their properties in replacing their ordinary isotopes in molecular solution.

A comparison of the results shown in Table I for indefinite potentials, and those obtained by von Hevesy for definite potentials, leads to the interesting conclusion for all the metals tested, except in the case of zinc, that indefinite potentials are more negative than definite ones. In the particular case of copper this was found to hold by Hevesy as already indicated; but the data given in Table II definitely suggest the general applicability of the result. The values of the indefinite potentials shown have been deduced from the results shown in Table I, using the curves given by von Hevesy[1] showing the percentage of the isotope of bismuth and lead respectively of the total quantity deposited on the electrode, and the potential required to bring about deposition.

TABLE II

Metal.	Zinc.	Tin.	Lead.	Copper.	Silver.	Platinum
Normal potential (against calomel electrode.)	−1.05	−0.43	−0.41	+0.06	+0.51	+0.6
Indefinite potential Metal | Water deduced from von Hevesy's curve from results of Table I.	−0.69	−0.50	−0.59	−0.42	−0.41	+0.01
Difference in Volts.	+0.36	−0.07	−0.18	−0.48	−0.92	−0.59

---

[1] Phil. Mag., (6) **23**, 637 (1912).

II

Re-determination of the Half-Life Period of Radium E

This re-determination was considered advisable in view of the fact that Bastings[1] in 1924, obtained the value 4.98 days, which differed very appreciably from the commonly accepted value 4.85 days as obtained by Thaller[2] in 1912, and suggested that the earlier value of 5.0 days as determined by Antonoff[3] was the correct one. It was therefore thought desirable to re-determine the period, and the above experiments involving electrodeposition on metallic plates suggested a suitable method of obtaining radium E in a state of purity. Recently, however, Fournier[4] has published his determination of the period as 4.86 days, also confirming Thaller's value: but since the experiment described in this paper, although akin in nature to Fournier's method, was undertaken before Fournier's results were advanced, and since the two determinations agree well, it may be useful to give a few details.

It was remarked above that the deposit obtained on a nickel plate consisted of practically pure radium E, and it was thought that if to the active solution a quantity of lead nitrate were added, the lead would mask the slight deposition of any radium D, and so a very pure deposit of radium E would be obtained.[5] This proved to be the case, and nickel plates so treated, measured after the lapse of two months were quite inactive, proving that radium E alone has been deposited.

In the active solution a quantity of lead nitrate was dissolved, and the pure nickel plate boiled with this solution for two hours, the plate being afterwards washed in water and then in alcohol to remove any adhering solution. Measurements of the activity were made as before with a beta-ray electroscope. The usual precautions of daily standardisation with a constant betaray source, and checking of the constancy of the natural leak were observed. The electroscopic measurements are considered to have an accuracy of about 1 in 300. Three determinations were made: two of these gave a value of 4.9 days to the degree of accuracy indicated, while the other, for which the electroscope was most thoroughly cleaned, and the insulation renewed, gave the value 4.87 days, which is in striking agreement with Fournier's value of 4.86 obtained by measurement with an accurate piezo-electrometer. Details of this last experiment are given in Table III, in which column A gives the activities as measured and column B contains those calculated on the basis of a half-life period of 4.87 days. The agreement between the experimental and theoretical values is very good.

---

[1] Phil. Mag., (6) **48**, 1075 (1924).

[2] Wien. Ber., **121**, 1611 (1912).

[3] Phil. Mag., (6) **19**, 825 (1910).

[4] Compt. rend., **181**, 502 (1925).

[5] Cf. Meyer and von Schweidler: Jahrb. Rad. Elektron, **3**, 381 (1906); **4**, 112 (1907).

TABLE III

Time in days	Activity in arbitrary units. A. Experimental.	B. Theoretical for period of radium E 4.87 days.
0.0	35.0	35.0
0.92	30.6	30.7
1.93	26.5	26.6
2.96	22.7	23.0
3.71	20.6	20.6
4.71	18.1	17.9
5.92	14.9	15.0
7.96	11.3	11.3
14.0	4.8	4.8
46.0	nil.	nil.

It is therefore evident that the above results, taken along with Fournier's work, indicate that Thaller's value of 4.85 days as the half-life period of radium E is the most accurate value yet available.

Synopsis

The results enumerated in this paper may be summarised as follows:—

1. The work of von Hevesy on the deposition of radioactive isotopes of bismuth and of lead on metals when the metals are dipped into solutions containing their own ions, has been extended to the case of metals dipping into pure water. The isotopes of bismuth and of lead used were radium E and radium D respectively. It has been found that these isotopes are deposited on metals irrespective of whether the latter are more electropositive or electronegative than bismuth or lead. It has also been found that the ratio of radium D to radium E deposited on metals decreases with the increasing electronegativeness of the metals, which is in qualitative agreement with Hevesy's results for definite potentials.

2. Aluminium and nickel, when boiled with pure neutral solutions of radium D and radium E, extracted radium E practically pure.

3. A re-determination of the half-life period of radium E has been made, and the value 4.87 days obtained, which confirms Thaller's value of 4.85 days.

The Radiometric Laboratory,
The University,
Glasgow.
February 2, 1926.

THE TRANSITION POINTS OF SALT HYDRATES IN NON-AQUEOUS SOLVENTS*

BY WALTER W. LUCASSE AND JOHN MCARTHUR HARRIS, JR.

A number of methods have been used to determine the transition points of various systems, the methods depending both upon abrupt changes and upon identity of certain properties at this point. For individual cases an especial method may be particularly applicable. Electrical methods have certain advantages[1] and have been used in a number of types of systems.

Electromotive force methods may depend in part either upon the difference in the ionic concentration in the saturated solution of the substance in the two phases or upon the change in the sign of the electromotive force while the system passes thru a series of temperatures where first the one and then the other phase is stable. Conductance methods may depend either upon a difference in the conductance of the two phases or upon a change in conductance due to a difference[2] in the solubility of the two phases. These methods, first used by Cohen, have recently been extended by Mason and Mathews[3] to non-aqueous systems where solvates are formed such as those with copper chloride and cadmium chloride in pyridine. In the case of salt hydrates we may take advantage, also, of the difference in conductance in a non-aqueous and in a mixed solvent. The results of such a study are given in the present paper.

Apparatus, Materials and Method

The cell used, except for certain preliminary runs and for the determinations with barium acetate, was in the shape of a large U-tube. In one arm the electrodes were permanently fixed while the other bore a thermometer, calibrated to tenths of a degree, which had been checked with a standard thermometer. This arrangement permitted the cell to be shaken without danger of changing the cell constant due to changing the relative position of the thermometer and electrodes.

The absolute alcohol was prepared by allowing ordinary commercial alcohol to stand over freshly broken lime for about two weeks during which time it was shaken several times each day. It was then distilled over a slow water bath, only the middle portion being retained. The salts used were all high-grade products and no attempt was made to further purify them.

In making a determination an excess of the salt was shaken with a quantity of the absolute alcohol at room temperatures. After being allowed to settle completely, the supernatant liquid was poured into the cell. The cell was then placed in a water bath which had been brought up to a temperature a few degrees below the transition point of the salt. The temperature of the bath was raised at the rate of about eight degrees an hour, and frequent readings of the resistance were made, the cell and contents being thoroughly shaken before each. The reading of the thermometer within the cell was noted simultaneously with the taking of the resistance.

---

*Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[1] Van't Hoff-Cohen: "Studies in Chemical Dynamics"; Findlay: "The Phase Rule."

[2] Svedberg: Ann. Physik, (4) **49**, 437 (1916); Cohen: Z. physik. Chem., **14**, 53 (1894).

[3] Mason and Mathews: J. Phys. Chem., **29**, 1507 (1925).

Results

In Table I are given the results obtained with calcium chloride showing the values of the resistance at the respective temperatures. In the first series are given the results obtained by using a solution made up as described above. Series 2 gives the results from a solution made up in the same manner but which was evidently slightly less concentrated. The third and fourth series give results from solutions which were made up by diluting with absolute alcohol portions of the same solution as used in Series 2, the former in the ratio of one part solution to three parts absolute alcohol, and the latter, one part solution to nine parts absolute alcohol. These results are plotted in Fig. 1 where the ordinates give the resistances and the abscissas, the temperatures. In each case a solid straight line is drawn thru the points below and above the transition point. In order to make the change more apparent the former

TABLE I

$CaCl_2.6H_2O = CaCl_2 . 4H_2O\beta + 2H_2O$

R = Resistance

Series 1		Series 2		Series 3		Series 4	
Temp.	R	Temp.	R	Temp.	R	Temp.	R
26.7	23.29	23.4	41.78	24.2	167.0	25.2	328.7
27.2	23.01	24.2	41.20	24.7	166.0	25.8	327.0
27.5	22.77	24.8	40.69	25.4	165.0	26.3	325.5
27.9	22.45	25.5	40.11	26.1	163.8	26.8	323.8
28.5	22.07	26.2	39.55	26.9	162.3	27.4	322.4
29.2	21.70	26.8	39.23	27.4	161.1	27.6	321.5
29.5	21.41	27.4	38.77	28.2	159.7	28.3	319.9
30.0	21.03	28.1	38.23	29.4	158.2	28.8	318.3
30.5	20.83	28.8	37.73	29.8	157.3	29.2	317.0
31.0	20.56	29.2	37.47	30.4	156.5	29.6	316.1
31.5	20.34	29.5	37.24	31.2	155.4	30.1	315.2*
32.1	19.99	30.0	36.93	31.6	154.6	30.9	313.0
		30.4	36.71	32.3	153.7	31.4	311.5
		31.1	36.30	32.9	152.7	32.0	310.1
		31.8	35.81	33.8	151.7	32.6	308.5
		32.1	35.64				
		32.7	35.25				
		33.2	34.97				
		33.6	34.86				
		34.1	34.46				

is continued above the transition point as a broken line. While the individual points fail to lie as closely upon the curves in some cases as might be desired, there can be no doubt considering all of the points that such a break occurs and that it takes place at about the accepted transition point. The deviations are due, no doubt, to the method of temperature control. In certain preliminary determinations where the solution was very concentrated or not made up immediately before carrying out the measurements an additional break seemed to appear at about 32°. This may have been due to experimental error or to the results of compound formation between the solvent and solute.

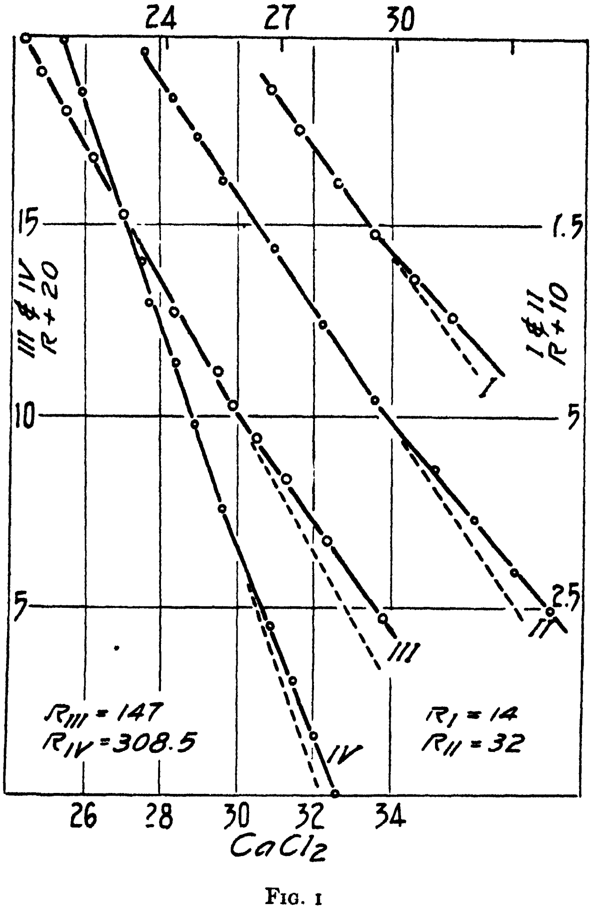


FIG. 1

In Table II are given the results with lithium nitrate, the first series being those from a saturated solution made up as described above and the second from a solution made up by diluting one part of the saturated solution with three parts of absolute alcohol. The difference in the resistance temperature

TABLE II

$LiNO_3 . 3H_2O = LiNO_3 . \frac{1}{2}H_2O + 2\frac{1}{2}H_2O$

R = Resistance

Series 1		Series 2	
Temp.	R	Temp.	R
24.1	35.28	25.0	51.57
24.8	34.79	25.6	51.14
25.7	34.33	26.2	50.63
26.3	34.03	26.7	50.19
27.2	33.49	27.1	49.85
27.9	33.04	27.7	49.31
28.7	32.50	28.5	48.71
29.3	32.00*	29.1	48.32
30.2	31.58	29.5	47.91
30.9	31.10	30.1	47.46
31.6	30.65	30.6	47.08
32.1	30.27	31.1	46.74
		31.6	46.48
		32.2	46.07
		32.7	45.66
		33.2	45.17
		33.8	44.94
		34.2	44.60

TABLE III

$Ba(C_2H_3O_2)_2, H_2O = Ba(C_2H_3O_2)_2 + H_2O$

R = Resistance

Series 1		Series 2	
Temp.	R	Temp.	R
25.4	39920	31.3	13550
31.2	37520	32.8	13260
32.6	36780	35.2	12910
35.1	35760	38.7	12360
38.5	34490	40.2	12150
40.0	33660	40.9	12020
40.8	33260	41.7	11950
41.5	32990	42.6	11810
42.5	32730	43.8	11680
43.6.	32070	44.8	11480
44.7	31810	47.3	11220
47.2	31050	49.1	10960
49.0	30180		

coefficients of these two solutions as shown from the results plotted in Fig. 2 is due, no doubt, to the difference in the solvation of the ions in the two solutions. The change in the slope of the two curves upon passing thru the transition point is of about the same order of magnitude but of opposite sign. In the more concentrated solution the decrease in resistance per degree is greater above the transition point than below while in the less concentrated solution the reverse is the case. This effect of concentration does not seem to exist in the solutions of calcium chloride, the difference being due, perhaps, to the different tendencies of the lithium and calcium ions toward solvation.

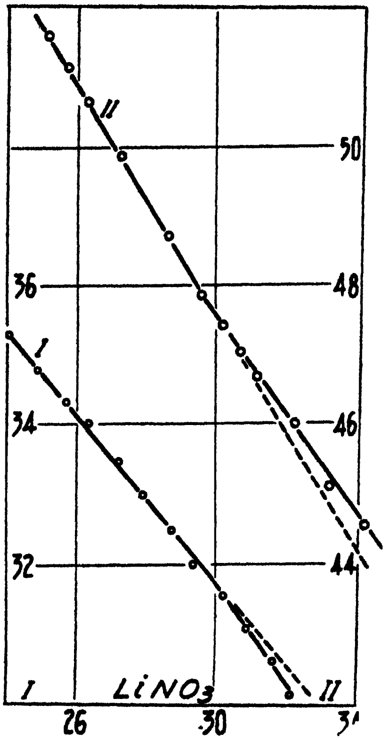


FIG. 2

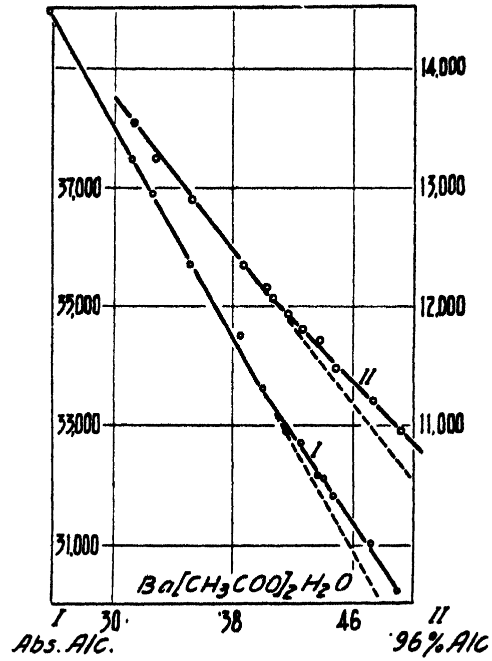


FIG. 3

In Table III and Fig. 3 are given the results of saturated solutions of barium acetate in absolute and in 96% alcohol. The slight water content in the latter solution increases the solubility and thus the conductance. Altho the value of the transition point of a particular system as determined by different methods may vary considerably, it is not likely that changing the solvent or modifying it slightly as in the present case would have any marked effect. The order of accuracy obtained with this particular salt was not such as to permit any conclusions to be drawn in this respect from the different values obtained from the calculations given below.

In Table IV are given the results from saturated solutions[1] of strontium nitrate (31.3°) and calcium bromide made up in the manner described. The curves are plotted in Fig. 4 where it is seen that the intersections of the curves come at about the accepted values of the transition points.

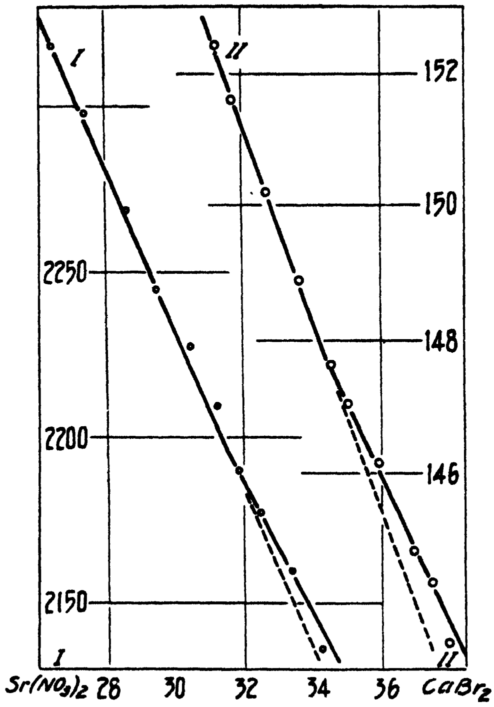


FIG. 4

TABLE IV

$Sr(NO_3)_2 . 4H_2O = Sr(NO_3)_2 + 4H_2O$ R = Resistance		$CaBr_2 . 6H_2O = CaBr_2 . 4H_2O + 2H_2O$ R = Resistance	
	Series 1		Series 2
Temp.	R	Temp.	R
26.3	2318	31.1	152.4
27.3	2299	31.6	151.6
28.5	2269	32.6	150.2
29.4	2245	33.2	149.3
30.4	2228	33.6	148.9
31.2	2210	34.0	148.6*
31.8	2190	34.5	147.6
32.4	2177	35.0	147.0
33.3	2160	35.9	146.1
34.2	2136	36.9	144.8
		37.4	144.3
		37.9	143.4

---

[1] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 3, 849 (1923).

Calculation of the Transition Point

The curves showing the resistances of these systems as a function of the temperature are doubtlessly slightly curved rather than straight as indicated in the diagrams. However, over the small temperature range above and below the transition point, they may be considered straight within experimental error. On this assumption we may calculate the transition point by determining the equations of the two curves for each system. The intersection of the two curves gives the transition point since here the resistance becomes the same. The constants of the equations

$$R=a+bt$$

were determined by the method of least squares and are given in Table V. In the first column is given the formula of the salt followed by the reference to the table and series where the data are given from which the constants of the equation were determined. The constants *a* and *b* are given in the second and third columns and refer to the equation below the transition point. The constants a′ and b′ are for the corresponding curve above the transition point. Solution of the equations for *t* yields the values of the transition points given in column six. In the last column are given values obtained by other methods. In the tables above all points obtained in the temperature interval are given. In determining the equations of the curves, however, a few points were omitted if from the plot they were seen to be in error. This was done particularly when such a point lay at or near the end of the curve and would thus, due to the small number of points, have a considerable effect on the slope of the curve. The legitimacy of disregarding these points may well be seen from the curves with strontium nitrate. Inclusion of the points at 30.4° and 31.2° would not only wipe out the self-consistency of the earlier points but would so change the slope of the curve as to make the points at higher temperatures

TABLE V

Calculation of the Transition Points

Salt		a	b	a′	b′	t	t′
$CaCl_2$	I, 1	41.04	−0.6652	36.76	−0.5216	29.8	29.2[1]
	I, 2	59.09	−0.7419	55.01	−0.6021	29.2	29.2
	I, 3	209.1	−1.743	200.1	−1.435	29.2	29.2
	I, 4	401.6	−2.895	391.04	−2.531	29.1	29.2
$LiNO_3$	II, 1	49.47	−0.5894	52.10	−0.6796	29.2	29.6[2]
	II, 2	71.93	−0.8139	68.45	−0.6973	29.8	29.6
$Ba(Ac)_2$	III, 1	50803.0	−427.9	48152.0	−365.3	42.4	41.0[3]
	III, 2	18408.0	−156.1	17417.0	−131.5	40.3	41.0
$CaBr_2$	IV, 2	196.46	−1.418	189.04	−1.200	34.0	34.2[4]

---

[1] Bancroft: "The Phase Rule," 71 (1897).

[2] Donnan and Burt: J. Chem. Soc., **83**, 335 (1903).

[3] Walker and Fyffe: J. Chem. Soc., **83**, 173 (1903).

[4] Landolt-Börnstein Tabellen, I, 641 (1923).

without meaning. Points omitted in the calculation are indicated in the tables by an asterisk; the remaining points were given equal weight. If from the graph a point appeared to lie at the intersection of the lines it was included in the calculation of both curves.

From a study of the four curves for the different concentrations of calcium chloride it appeared that the curves intersected at about 29.5°. This point was used therefore as a basis for calculating the two curves in each case, the points lying to either side of this value being used to determine the equation. This proceedure gave values of 29.2° and 29.1° for the transition point of the three dilute solutions and 29.8° for the most concentrated solution. The transition point of the system $CaCl_2 . 6H_2O$ in equilibrium with $CaCl_2 . 4H_2O\beta$ is given as 29.2° and for $CaCl_2 . 6H_2O$ with $CaCl_2 . 4H_2O\alpha$ as 29.8°. It would appear therefore that in the less concentrated solutions, at least, it is the β tetrahydrate which is formed. That the unstable modifidation rather than the α tetrahydrate is formed may be due to the solvent. It will be recalled that crystals of $Na_2SO_4 . 7H_2O$ can be obtained by adding alcohol to a mixture of sodium sulphate and water.

It may be seen from the values of the transition points given in the last two columns of the table that the values obtained by the present method agree within somewhat better than 0.3 of a degree, except in the case of barium acetate, with those obtained by other methods. This agreement is as good as could be expected in view of the order of accuracy sought. It might be advantageous to hold the system at a series of temperatures below and above the transition point, as is usually done, rather than to attempt to take instantaneous readings of the variables.

Discussion

Preliminary determinations were made with a number of other systems and in each case the transition point came at about the temperature found by other methods. Thus, runs were made with zinc sulphate in absolute alcohol and in 96% alcohol; cadmium chloride in absolute alcohol, and sodium sulphate containing various amounts of water. The cadmium salt under certain conditions formed a gel with the alcohol and thus limited its use. The solubility of sodium sulphate in absolute alcohol is so slight that no break could be detected. With the addition of from 2 to 4% water the solubility increases sufficiently so that a change in the slope of the curve at the transition point was easily observable. With larger amounts of water the break seemed to disappear. Altho these and other determinations indicate the generality of the phenomenon, the accuracy sought was not sufficient to warrant the calculation made above.

It was hoped that the present study might throw some light upon the problem of complete and partial dissociation. In its present form, however, this does not seem to be the case. The phenomena involved are too many and too complicated to permit of ready interpretation. We may believe that the undissociated parts of dissolved salts are hydrated to about the same extent as in the solid state at the same temperature and thus that the change in the temperature resistance curve above the transition point[1] is due to the changes in the properties of the system caused by the liberation of the molecules of water from the undissociated salt. Or, we may believe that the salt upon dissolving becomes completely dissociated and that the water molecules in part, at least, become associated with the ions, and further that at the transition point the ions become somewhat less hydrated. Thus no definite view can be formed from these experiments relative to the extent of dissociation. In either case one might expect a somewhat abrupt change in the magnitude of the conductance at the transition point after which there would appear a change in slope due to the different temperature coefficients. This, however, was not borne out, due perhaps, to the very slight change in the viscosity and dielectric constant of the solvent. Interpretation is further complicated by the presence of two molecular species either of which may contribute to the solvation of the ions.

The method might be extended to other solvents. Obviously the most advantageous system with which to work would be one in which a highly hydrated salt is very soluble in a solvent of low dielectric constant. Such a system, however, by the nature of solubility is obviously not possible to find. In general for a particular system we should expect the difference in the slopes of the curves to diminish with increasing dilution. This is seen to be the case with the results given above for barium acetate and for calcium chloride. For the four concentrations in the latter case the ratio of the slopes of the curves above and below the transition point are, with increasing dilution, 1.28, 1.23, 1.21 and 1.14.

Summary

The above study indicates that even tho dissolved a measurable change takes place at the transition points of salt hydrates.

Values of the transition points of certain salts from a study of the resistance temperature curves of their solutions in alcohol are given.

The results were obtained by calculating the intersection of the two curves resulting from the difference in the slopes of the curves below and above the transition point.

Philadelphia,
Pennsylvania.

---

[1] Arrhenius: "Theories of Solutions" (1912).

CATALYTIC AND INDUCED OXIDATION OF SOME CARBOHYDRATES, URIC ACID, AND INORGANIC SUBSTANCES

BY C. C. PALIT AND N. R. DHAR

In foregoing publications,[1] we have shown that many substances which are not ordinarily oxidised by air, are readily oxidised by air in presence of reducing agents like sodium sulphite, ferrous hydroxide, cerous hydroxide, manganous hydroxide, phosphorus, iron, cuprous oxide, stannous chloride, etc.

In a previous paper[2] we have shown that solutions of different carbohydrates can be oxidised by passing air at the ordinary temperature in presence of cerous hydroxide. We have observed that in presence of an excess of alkali, carbohydrates like starch, maltose, arabinose, laevulose, galactose, glucose, lactose and cane sugar can be completely oxidised by passing air for about five and a half hours in presence of cerous hydroxide, which undergoes oxidation. In the same paper we also published some preliminary results on the oxidation of maltose and lactose by passing air in presence of freshly precipitated ferrous hydroxide.

In this paper we have investigated the oxidation of starch, maltose, laevulose, lactose, arabinose, cane sugar, galactose and glucose by air in presence of sodium sulphite or freshly precipitated ferrous hydroxide. Moreover we have investigated the oxidation of uric acid, sodium arsenite, arsenious acid, sodium nitrite and potassium oxalate in presence of various substances.

The experimental method adopted in this communication is the same as that described in the paper by Palit and Dhar.[3] The experimental results are obtained in the oxidation of the carbohydrates are given in Tables I-III.

(2)—Uric Acid

After having made a detailed investigation on the oxidation of carbohydrates by passing air in presence of different reducing agents, we have naturally started investigation on the oxidation of some nitrogenous matter, and the first substance chosen is uric acid. The uric acid was estimated by potassium permanganate. Standard solution of uric acid was made by weighing a known amount of the substance and dissolving it in dilute solution of caustic soda and making it up to a definite volume. 10 c.c. of this standard solution

---

[1] Dhar: Proc. Akad. Wet. Amsterdam, **29**, 1023 (1921); Mittra and Dhar: Trans. Faraday. Soc., **17**, 676 (1922); Z. anorg. Chem., **122**, 146 (1922); J. Phys. Chem., **29**, 376 (1925).

[2] Palit and Dhar: J. Phys. Chem., **29**, 799 (1925).

[3] loc. cit.

Carbohydrates

TABLE I

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ solution used was 20 c.c.[$=0.0674$ grm. of $Fe(OH)_2$].

No. of Expt.	Carbohydrate used for the experiment.	Actual weight of carbohydrate in 10 cc. of the solution taken in grm.	Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing										
			(1) 0 075	(2) 0.10	(3) 0.15	(4) 0.20	(5) 0.25	(6) 0.30	(7) 0.35	(8) 0.40	(9) 0.50	(10) 0.60	(11) 0.70
1	Starch	0.1027	0.0485	0.0523	0.0573	0.0636	0.0932	0.0973	0.1013	0.1021	Complete oxidation		
2	Maltose	0.1097	0.0323	0.0516	0.0779	0.0829	0.0849	0.0943	0.0999	—	do	do	
3	Lactose*	0.0997	0.0164	0.0258	0.0388	0.0797	0.0832	0.0926	0.0992	—	do	do	
4	Laevulose*	0.09185	0.0155	0.0202	0.0345	0.0462	0.0567	0.0651	0.0756	—	do	do	
5	Arabinose	0.1000	0.0040	0.0138	0.0218	0.0254	0.0321	0.0411	0.0904	—	do	do	
6	Cane Sugar	0.0964	0.0204	0.0134	0.0185	0.0078	0.0043	0.0079	0.0281	0.0158	0.0087	0.0054	0.0016
7	Galactose	0.0861	0.00965	0.0112	0.0128	0.0152	0.0246	0.0349	0.0487	—	0.0703	0.0802	0.0821
8	Glucose	0.0962	0.00235	0.0066	0.0129	0.0172	0.0493	0.0599	0.0698	0.0768	0.0873	0.0935	complete oxidation

*These results have been taken from our previous publication. Palit and Dhar: J. Phys. Chem. **29**, 799 (1925).

TABLE II

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of Sodium Sulphite taken was 20 c.c.[=0.1513 grm. of Na_2SO_3].

No. of Expt.	Carbohydrate used for the experiment.	Actual weight of carbohydrate in 10 cc. of the solution taken in grm.	Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing										
			(1) 0.00	(2) 0.10	(3) 0.15	(4) 0.20	(5) 0.25	(6) 0.30	(7) 0.35	(8) 0.40	(9) 0.50	(10) 0.60	(11) 0.70
1	Starch	0.1027	0.0273	0.0213	0.0221	0.0430	0.0586	0.0183	0.0214	0.0326	0.0200	0.0247	0.0231
2	Maltose	0.1097	—	0.0300	0.0381	0.0446	0.0501	0.0568	0.0607	—	0.0349	0.0337	0.0307
3	Lactose	0.0997	0.0250	0.0084	0.0116	0.0173	0.0245	0.0275	0.0305	—	0.0354	0.0345	0.0326
4	Laevulose	0.09185	0.0000	0.0007	0.0014	0.0018	0.0067	0.0194	0.0214	—	0.0256	0.0387	0.0427
5	Arabinose	0.1000	0.0096	0.0041	0.0072	0.0098	0.0252	0.0395	0.0524	—	0.0286	0.0365	0.0363
6	Cane Sugar	0.0964	0.0099	0.0034	0.0008	0.0125	0.0153	0.0146	0.0015	0.0082	0.0210	0.0232	0.0150
7	Galactose	0.0861	0.0104	0.0047	0.0047	0.0123	0.0318	0.0443	0.0169	0.0367	0.0660	0.0773	0.0764
8	Glucose	0.0962	0.0088	0.0033	0.0057	0.0062	0.0133	0.0302	0.0048	0.0217	0.0497	0.0708	0.0699

TABLE III

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours.

No. of Expt.	Carbohydrate used for the experiment.	Actual weight of carbohydrate in 10 cc. of the solution taken in grm.	Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing								
			(1) 0.00	(2) 0.05	(3) 0.075	(4) 0.10	(5) 0.15	(6) 0.20	(7) 0.25	(8) 0.30	(9) .035
1	Starch	0.1027	0.0000	0.0310	—	0.0364	0.0241	—	0.0245	—	0.0255
2	Maltose	0.1097	—	—	—	—	—	—	—	—	—
3	Lactose	0.0997	—	—	—	—	—	—	—	—	—
4	Laevulose	0.09185	—	—	—	—	—	—	—	—	—
5	Arabinose	0.1000	0.0000	0.0109	—	0.0254	0.0365	—	0.0403	0.0485	0.0561
6	Cane Sugar	0.0964	0.0000	0.0125	—	0.0119	0.0121	—	0.0122	—	0.0120
7	Galactose	0.0861	0.0000	0.0017	—	0.0080	0.0169	0.0267	—	—	—
8	Glucose	0.0962	0.0000	0.0109	—	0.0686	—	0.0807	—	—	—

were taken in each case and mixed with freshly precipitated hydroxides of the respective metals. The results are given in Table IV.

TABLE IV

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of uric acid added was 10 cc [= 13.0 cc. y N/10 $KMnO_4$ = 0.0975 grm of uric acid]. The different metallic salt solutions were precipitated by an equivalent amount of alkali and the resulting mixture was practically neutral.

No. of Expt.	Substance added as catalyst.	Amount of catalyst present in grm. per c.c.	Amount of uric acid oxidised in grm. in presence of different catalysts containing the following volumes in c.c.			
			10	20	40	50
1.	Ferrous Sulphate	0.01 grm of salt	0.0060	0.0120	0.0120	
2.	Manganese Nitrate	0.0115 grm "	0.0390	0.0600		0.0727
3.	Cerium Chloride	0.01 grm "	0.00975	0.0210		
4.	Cobalt Nitrate	0.01 " "			0.05325	
5.	Nickel Nitrate	0.01 " "			0.03375	
6.	Copper Nitrate	0.025 " "			0.0810	
7.	Sodium Sulphite	0.00757 " "	0.01275	0.0225	0.0525	
8.	Caustic Soda	0.005 gr of NaOH	0.0075	0.00975		

The experimental results show that in presence of alkali, uric acid is appreciably oxidised by passing air in absence of any catalyst. In presence of hydroxides of different metals, the oxidation of uric acid is increased and the order of the accelerating effect of the different catalysts is the following:—

Cupric > manganous > cobaltous > sodium sulphite > nickelous > cerous > ferrous

3(a)—Sodium Arsenite

We have also determined the oxidation of arsenious acid and of sodium arsenite by passing air in presence of alkali and hydroxides of different metals. The results are given in Tables V-VII.

These results indicate that no oxidation of Sodium Arsenite or arsenious acid takes place in aqueous solution or in presence of alkali.

From our experimental results it will be seen that sodium arsenite even in presence of an excess of alkali cannot be oxidised by passing air.

TABLE V

Experiments with Sodium Arsenite in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium arsenite used was 10 c.c. in each case [10 c.c. of sodium arsenite solution≡10.0 c.c. of N/10 Iodine]

No. of Expt.	Substance added as catalyst	Amount of catalyst added in grm	Amount of caustic soda added in grm.	Volume in c.c. of N/10 Iodine required for 10 c.c. of sodium arsenite taken	Volume in c.c. of N/10 Iodine required for 10 sodium Arsenite left after the experiment	Amount of Sodium Arsenite oxidised in terms of N/10 Iodine in c.c.
1	Cobalt Nitrate	0.20 grm.	0.20	10.0	7.4	2.6 c.c.
2	Nickel Nitrate	0.20 "	"	"	4.6	5.4 c.c.
3	Manganese Nitrate	0.230 "	"	"	2.6	7.4 c.c.
4	Mercuric Chloride	0.20 "	"	"	0.3	9.7 c.c.
5	Copper Nitrate	0.504 "	"	"	1.9	8.1 c.c.
6	Lead Nitrate	0.20 "	"	"	2.8	7.2 c.c.
7	Uranium Chloride	0.20 "	"	"	4.8	5.2 c.c.
8	Mercurous Nitrate	0.27 "	"	"	0.2	9.8 c.c.
9	Ferrous Sulphate	0.20 "	"	"	7.6	2.4 c.c.
10	Ferric Chloride	0.122 "	"	"	8.9	1.1 c.c.

3(b)—Arsenious Acid

TABLE VI

Experiments with Arsenious Acid in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of arsenious acid used was 10 c.c. in each case [10 c.c. of Arsenious Acid≡9.55 c.c. of N/10 Iodine].

No. of Expt.	Substance added as catalyst	Amount of catalyst added in grm	Amount of caustic soda added in grm.	Volume in c.c. of N/10 Iodine required for 10 c.c. of arsenious acid taken	Volume in c.c. of N/10 Iodine required for arsenious acid left after the experiment	Amount of arsenious acid oxidised in terms of N/10 Iodine in c.c.
1	Cobalt Nitrate	0.20 grm.	0.20	9.55	8.0	1.55
2	Nickel Nitrate	0.20 "	"	"	4.0	5.55
3	Manganese Nitrate	0.23 "	"	"	1.5	8.05
4	Mercuric Chloride	0.20 "	"	"	0.3	9.25
5	Copper Nitrate	0.504 "	"	"	0.7	8.85
6	Lead Nitrate	0.20 "	"	"	3.0	6.55
7	Mercurous Nitrate	1.024 "	"	"	0.6	8.95
8	Ferrous Sulphate	0.20 "	"	"	7.6	1.95
9	Ferric Chloride	0.122 "	"	"	7.75	1.80
10	Uranium Chloride	0.20 "	"	"	3.8	5.75
11	Cuprous Chloride	0.07 "	"	9.55	0.65	8.90

TABLE VII

Experiments with Sodium Arsenite and arsenious acid in presence of alkali. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium arsenite or arsenious acid taken was 10 c.c. in each case.

No. of Expt.	Substance used in the experiment	Volume in c.c. of the solution of substance taken	Volume of N/10 Iodine required for the substance taken	Volume of N/10 Iodine in c.c. required for the substance taken in presence of caustic soda containing in grm.					Amount of substance oxidised
				(1)	(2)	(3)	(4)	(5)	
1	Sodium Arsenite	10.0	10.0	10.0	10.0	10.0	10.0	10.0	Nil
2	Arsenious Acid	10.0	9.55	9.55	9.55	9.55	9.55	9.55	Do

On the other hand sodium arsenite becomes oxidised when air is passed through a solution of the substance in contact with different hydroxides. The order in which the hydroxides accelerate the reaction is as follows:—

Mercurous, > mercuric > cuprous > cupric >, manganous > lead >, nickelous >, uranium >, cobalt >, ferrous > ferric.

In a recent paper Reinders and Vles[1] have shown that cupric salts act as positive catalysts in the oxidation of sodium arsenite by air. The above authors have not observed any accelerating effect of other salts.

In a previous paper Mittra and Dhar[2] have proved that the oxidation of sodium sulphite by air is retarded by the presence of sodium nitrite. In the same paper it was shown that marked retardation of the oxidation of sodium sulphite by air takes place in presence of potassium oxalate. These results are in agreement with our generalisation that reducing agents act as negative catalysts in oxidation reactions.

In a subsequent paper we[3] have attempted to induce the oxidations of sodium chromite, sodium manganite, sodium nitrite and potassium oxalate by passing air in contact with cerous hydroxide. Only sodium chromite and sodium manganite were partially oxidized to sodium chromate and sodium manganate respectively. Sodium nitrite and potassium oxalate were not appreciably oxidized. Similar results have very recently been obtained by Jorissen and van der Pol[4].

We have made further careful experiments in the oxidation of sodium nitrite and potassium oxalate by air in presence of different catalysts. The results are given in Tables VIII-X.

---

[1] Rec. Trav. chim., **44**, 29 (1925).

[2] J. Phys. Chem., **29**, 376 (1925).

[3] Palit and Dhar: loc. cit.

[4] Rec. Trav. chim., **44**, 805 (1925).

(4) Sodium Nitrite

TABLE VIII

In this experiment the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ used was 20 c.c.[≡0.06476 gr. of $Fe(OH_2)$] and the volume of Na_2SO_3 used was also 20 c.c.≡[0.1513 gr of Na_2SO_3]. Also 20 c.c. of $FeSO_4$≡0.075 grm of NaOH.

No. of Expt.	The order in which the substances were taken	Actual amount of sodium nitrite in 10 cc. of the solution	Amount of sodium nitrite in grm. oxidised in presence of caustic soda containing in grm.						
			(1) 0.00	(2) 0.05	(3) 0.075	(4) 0.10	(5) 0.15	(6) 0.20	(7) 0.25
1	$FeSO_4$ $NaNO_2$ NaOH H_2O } Total volume =100 c.c.	0.0983 grm.	—	—	0.01145	—	0.0069	0.0060	—
2	$FeSO_4$ NaOH $NaNO_2$ H_2O } = 100 c.c.	do	—	—	0.0017	0.0007	Nil	Nil	Nil
3	Na_2SO_3 $NaNO_2$ NaOH H_2O } * = 100 c.c.	do [≡28.5 c.c. of N/10$KMnO_4$]	Nil (28.5 c.c.)	Nil (28.65c.c.)	— —	Nil (28.7 c.c.)	Nil (28.9 c.c.)	Nil (28.9 c.c.)	Nil (29.0 c.c.)

*In the case of sodium sulphite, the amount of potassium permanganate (N/10) required after the experiment is slightly greater than that required for 10 c.c. of sodium nitrite taken in a blank experiment. The figures within brackets indicate the volume of N/10 $KMnO_4$ required.

TABLE IX

Experiments with Sodium Nitrite in presence of several catalysts. The volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium nitrite used was 10 c.c. in each case [10 c.c. of sodium nitrite sol. ≡ 28.5 c.c. of N/10 $KMnO_4$].

1 No. of Expt.	2 Substance added as catalyst	3 Amount of catalyst added in grm.	4 Amount of caustic soda added in grm.	5 Volume in c.c. of N/10 $KMnO_4$ required for 10 c.c. of nitrite	6 Volume in c.c. of N/10 $KMnO_4$ required for the nitrite left after the experiment	7 Difference in volume of $KMnO_4$ between the numbers (5) and (6) positive and negative
1	(a) Ferrous Sulphate	0.05 grm.	0.25	28.5	28.5	0.0
	(b) do do	0.40 ”	0.16	do	25.8	−2.7 c.c.
	(c) ” ”	0.50 ”	0.20	do	25.6	−2.9 c.c.
2	Ferric Chloride	0.0305 ”	0.25	28.5	28.7	+0.2 c.c.
3	(a) Manganese Nitrate	0.0575 grm.	0.25	28.5	28.5	0.0 c.c.
	(b) ” ”	0.230 ”	0.105	do	28.7	+0.2 c.c.
	(c) ” ”	0.460 ”	0.210	do	28.7	+0.2 c.c.
	(d) ” ”	0.575 ”	0.2625	do	28.75	+0.25 c.c.
4	Cobalt Nitrate	0.20 grm.	0.0575	28.5	28.95	+0.45 c.c.
5	Nickel Nitrate	0.20 grm.	0.055	28.5	28.95	+0.45 c.c.
6	Chromium Sulphate	0.20 grm.	0.070	28.5	28.6	+0.1 c.c.
7	Mercuric Chloride	0.20 grm.	0.060	28.5	28.9	+0.4 c.c.
8	Copper Nitrate	0.126 grm.	0.25	28.5	28.8	+0.3 c.c.
	(b) ” ”	0.504 ”	0.215	do	do	+ do
	(c) ” ”	1.260 ”	0.5375	do	28.9	+0.4 c.c.
9	(a) Cerium Chloride	0.40 grm.	0.20	28.5	28.9	+0.4 c.c.
	(b) ” ”	0.50 ”	0.25	28.5	28.95	+0.45 c.c.

(5) Potassium Oxalate

TABLE X

In this experiment the volume of air passed was 36.5 litres in 5.5 hours and the volume of $FeSO_4$ used was 20 c.c. [≡0.06476 grm. of $Fe(OH)_2$] and the volume of Sodium Sulphite was 20 c.c. [≡0.1513 grm. of Na_2SO_3]. Also 10 c.c. of potassium oxalate solution ≡ 10.8 c.c. of N/10 $KMnO_4$.

No. of Expt.	Substance added as catalyst	Volume of N/10 $KMnO_4$ required in c.c. for 10 c.c. of potassium of solution	Volume of N/10 $KMnO_4$ in c.c. required after the experiment in presence of caustic soda containing in grm.						
			(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	Ferrous Sulphate	10.8	10.8	10.9	11.0	11.1	11.2	11.2	11.2
2	Sodium Sulphite	10.8	10.8	10.9	11.1	11.2	11.2	—	—

N. B. In each of these experiments the amount of potassium permanganate required after the experiment is greater than that required before the experiment.

According to Gmelin-Kraut,[1] Berzelius found a direct oxidation of nitrite to nitrate with air. On the other hand, Matignon and Marchal[2] were unable to show a direct oxidation. Our experimental results show that even in presence of alkali, sodium nitrite is not appreciably oxidized by air. Reinders and Vles[3] have observed no perceptible oxidation in neutral or alkaline sodium nitrite.

From our experimental results, it will be observed that when air is passed through freshly precipitated ferrous hydroxide containing sodium nitrite appreciable quantities of sodium nitrite are oxidised. This is a typical case of induced oxidation; the oxidation of ferrous hydroxide induces the oxidation of the nitrite.

When ferrous sulphate is added to a solution of sodium nitrite and then alkali is added, the amount of the oxidation of the nitrite is greater than that obtained when the nitrite is added to ferrous hydroxide which has already been precipitated by the interaction of ferrous sulphate and alkali. This is due to the fact that on the addition of ferrous salt to a nitrite, a basic nitrite is formed and nitrous acid is set free and a part of the nitrous acid immediately oxidises the ferrous salt to the ferric state with the formation of nitric oxide which in its turn is oxidised to nitrogen peroxide by air which reacts with water and forms nitric acid and nitric oxide. Moreover free nitrous acid undergoes decomposition according to the following reaction:—

$$3HNO_2 \leftrightharpoons HNO_3 + 2NO + H_2O$$

Hence apparently the amount of oxidation of nitrite is greater than in the previous case where the nitrite is added to the ferrous hydroxide which has already been precipitated.

We could not oxidise sodium nitrite by passing air in presence of $Fe(OH)_3$ $Cu(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$, $Cr(OH)_3$, $Ni(OH)_2$, Na_2SO_3, HgO and $Ce(OH)_3$. The hydroxides of the above metals were obtained in the freshly precipitated condition. It must be emphasised that these substances must be in the freshly precipitated condition, because we[4] have repeatedly observed that the chemical reactivity of a substance decreases with its age.

From our experimental results it will be seen that when air is passed through solution of potassium oxalate containing reducing agents, like $Fe(OH)_2$, $Ce(OH)_3$, Na_2SO_3, etc., there is appreciably no oxidation of the oxalate. On the other hand after removing the $Fe(OH)_3$, $Ce(OH)_4$ and unchanged Na_2SO_3, if the oxalate is titrated with $KMnO_4$ in presence of an excess of dilute H_2SO_4, greater quantities of $KMnO_4$ are required than that calculated in terms of oxalate originally taken. In the end of the titration the colour of $KMnO_4$ disappears very slowly.

Exactly similar results were obtained in the experiments on sodium nitrite in the presence of $Fe(OH)_3$, $Cr(OH)_3$, $Ni(OH)_2$, $Co(OH)_2$, $Ce(OH)_3$, $Mn(OH)_2$,

---

[1] Handbuch. anorg. Chem., 1 I, 271.

[2] Compt. rend., 170, 232 (1920).

[3] Rec. Trav. chim., 44, 1 (1925).

[4] Ganguli and Dhar: J. Phys. Chem., 26, 836 (1922); Chatterji and Dhar: Kolloid-Z. 33, 18 (1923); Ghosh and Dhar: J. Phys. Chem., 29, 432 (1925).

$Cu(OH)_2$ and HgO. It is difficult to explain this peculiar behaviour. It seems probable that some unstable oxidising agent like H_2O_2 is formed when air is passed through solutions of sodium nitrite or potassium oxalate in presence of the hydroxides and this unstable substance reacts slowly on $KMnO_4$. We are trying to elucidate the matter further. We have observed that when air is passed through solutions of sodium nitrite or potassium oxalate in the absence of the hydroxides, no such peculiar behaviour is observed.

From the foregoing results it will be observed that even in the absence of alkali all the eight carbohydrates can be oxidised by passing air through solutions of the carbohydrates in the presence of sodium sulphite or ferrous hydroxide which in its turn is being oxidised. We have also proved that in presence of an excess of alkali most of the carbohydrates can be oxidised by passing air at the ordinary temperature. When the carbohydrates are oxidised by air in presence of freshly precipitated ferrous hydroxide and when there is no excess of alkali starch is more readily oxidised than the other carbohydrates and the order in which they are oxidised in the following:—starch > maltose > lactose > laevulose > cane sugar > arabinose > galactose > glucose.

With sodium sulphite the order is starch > lactose > galactose > cane sugar > arabinose > laevulose.

From the foregoing results it will be also observed that in the presence of ferrous hydroxide the oxidation of the carbohydrates usually increases with the increase in the amount of alkali with the exception of cane sugar, in which case increase of alkali does not increase the amount of oxidation. With sodium sulphite the results are analomous; in certain cases there is an increase and other cases there is a decrease in the amount of oxidation of the carbohydrates as the quantity of alkali is increased.

In the oxidation of the carbohydrates in presence of sodium sulphite, we have determined the amount of soidum sulphite, which is oxidised during the course of the oxidation. The results are given in Table XI.

From the foregoing results it will be seen that in absence of alkalies sodium sulphite is completely oxidised when air is passed through different carbohydrates. In presence of alkali the oxidation of the sulphite is appreciably retarded and it is observed that the greater the amount of alkali added the greater is the retardation of the oxidation of the sulphite. These results seem interesting and they will be discussed later on.

In this connection it will be interesting to consider the influence of alkalies on the slow oxidation of substances in air. In the foregoing pages we have shown definitely that practically all carbohydrates can be appreciably oxidised by passing air through the solutions of the carbohydrates in presence of alkalies. Similarly we have observed that uric acid can be oxidised in presence of alkalies by passing air. Moreover it is well known that though a solution of pyrogallic acid is not oxidised by passing air, yet an alkaline pyrogallate takes up oxygen readily. Similar results are obtainable with

TABLE XI

Estimation of Sodium Sulphite after Oxidation

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of sodium sulphite used was 20 c.c.[≡ 0.15 13 grm of Na_2SO_3].

No. of Expt.	Carbohydrate in presence of which the experiment is performed.	Actual amount of carbohydrate in 10 c.c. of the solution.	Percentage amount of sodium sulphite oxidised in grm. in presence of caustic soda containing in grm.										
			(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
			0.0	0 10	0 15	0 20	0 25	0 30	0.35	0 60	0 50	0 60	0.70
1	Maltose	0.1097	—	—	—	—	—	—	—	—	—	—	—
2	Lactose	0.0997	100	93.3	82.6	0	0	0	0	0	—	0	0
3	Laevulose	0.09185	100	74.0	—	25.2	—	12.5	—	—	—	0	—
4	Arabinose	0.1000	100	55.6	23.3	17.6	0	0	0	—	0	0	0
5	Galactose	0.0861	100	72.9	59.3	52.1	30.9	—	28.6	16.3	—	—	—
6	Glucose	0 0962	100	72.9	—	69.6	59.5	39.1	20.4	20.0	—	—	—
7	Cane Sugar	0.0964	100	97.0	31.3	27.8	0	—	—	—	—	0	0
8	Starch	0.1027	100	83.3	52.1	—	25.0	—	—	—	12.5	2.1	0

other hydroxy-organic compounds. It seems very likely that pyrogallate ions and ions from other hydroxy-compounds are more readily oxidised by air than the undissociated substances. Moreover, though ferrous, cerous, cobaltous, and manganous salt solutions can absorb oxygen very feebly, yet the hydroxides of all these metals readily take up oxygen from air.

In a previous paper,[1] it has been proved that the induced oxidation of nickelous hydroxide due to the oxidation of ferrous, manganous, or cobaltous hydroxides by passing air goes on increasing up to a limiting value and then it decreases as the concentration of alkali is increased. Similar results were obtained by Gire[2] in the induced oxidation of sodium arsenite due to the oxidation of $Fe(OH)_2$. Very recently Reinders and Vles[3] have obtained similar results in the oxidation of sodium arsenite in presence of cupric hydroxide.

Moreover we have proved in a foregoing paper[4] that a solution of sodium sulphite, is more readily oxidised by air or oxidising agents like $HgCl_2$ or I_2 than sulphurous acid of equivalent strength. We[5] have also proved that sodium formate is more readily oxidised by $HgCl_2$, $AgNO_3$, Halogens, etc., than formic acid of the same concentration. We have proved that this behaviour is due to the fact that these oxidising agents react on the formate or sulphite ions and not on the undissociated substances. On the other hand, we have proved that the oxidation of oxalic acid, formic acid, tartaric acid, sulphurous acid etc. by $KMnO_4$ or $H_2Cr_2O_7$ takes place mainly between the undissociated substances.

We are of the opinion that ferrous, cerous, manganous, and chromous hydroxides are more readily oxidised than their salt solutions because these gelatinous hydroxides with large surface can adsorb oxygen molecules readily and these oxygen molecules react with the hydroxides quickly at the surface.

From our experiments on oxidation reactions, we have proved that substances which are not ordinarily oxidised by air can be oxidised by passing air through their solutions containing reducing agents like $Fe(OH)_2$, Na_2SO_3, P, Cu_2O etc. In this way we have been able to oxidise many substances, e. g. carbohydrates, various organic acids and their salts, nitrite, arsenite etc.

In foregoing papers[6] in discussing the results obtained by Spoehr we made the following observations:—

"Very recently Spoehr has oxidized sugars by passing air through solutions of sugars containing ferric or ferrous salts and phosphoric acid. It is well known that in presence of excess of phosphoric acid or disodium phosphate complex ferrous and ferric salts are formed. The ferrous complex can be readily oxidized to the ferric state and this oxidation induces the oxidation of sugar, starch, etc. The amount of sugar or starch oxidised will depend on the amount of ferrous salt oxidised and hence this is a typical case of induced reaction.

---

[1] Mittra and Dhar: J. Phys. Chem., **29**, 376 (1925).
[2] Compt. rend., **171**, 174 (1920).
[3] Rec. Trav. chim., **44**, 29 (1925).
[4] Dhar: Proc. Akad. Wet. Amsterdam, **23**, 479 (1920).
[5] Dhar: J. Chem. Soc., **111**, 707 (1917).
[6] Mittra and Dhar: J. Phys. Chem., **29**, 376 (1925); Palit and Dhar: loc. cit.

"Glucose and other hexoses are also oxidised by air in solutions containing disodium phosphate and methylene blue with the formation of carbon dioxide. This reaction is greatly accelerated by iron salts. Not only the hexose sugars are thus oxidised, but also sucrose, trehalose, mannitol, and glycerol.

"Spoehr has observed that ferric salts also are effective in the oxidation of hexoses by air, but iron in the ferrous condition is more active than iron in the ferric condition. We have already observed that complex ferrous phosphate is a very good reducing agent and that the oxidation of this substance induces the oxidation of sugar, glycerol, etc.

"With complex ferric phosphate the case is different as it cannot be oxidised further. We have observed that the complex is very slowly reduced by sugar, glycerol, etc. into the ferrous complex, which in its turn is readily oxidised to the complex ferric phosphate and this oxidation induces the oxidation of glycerol, sugars, etc., As the action of sugars, glycerol, etc. on the complex ferric phosphate is very slow, the amount of induced oxidation of sugars, glycerol, etc., is much less than the amount of induced oxidation with complex ferrous phosphate. That is why Spoehr got 0.5600 gr CO_2 from 1 gram ferrous sulphate and 0.5392 gr CO_2 from an equivalent weight of ferric suphate using the same quantities of glucose and sodium phosphate."

In a recent paper, Spoehr has made the following statements:—

"In strongly alkaline solution, glucose is oxidised by air, but these conditions have only remote physiological influence because it has not been possible to oxidise glucose with air in solutions of hydroxyl ion (OH') concentrations approximating those found in the living organism even in presence of iron salts or phosphates."

In view of our experimental results, the above remarks need correction, because we have been able to oxidise eight carbohydrates in practically neutral solutions by passing air through the solutions of the carbohydrates in contact with cerous hydroxide or ferrous hydroxide.

From our experimental results as recorded in this paper it will be clear that neutral solutions of eight carbohydrates, uric acid, sodium nitrite, sodium arsenite etc., can be oxidised in presence of $Fe(OH)_2$, $Ce(OH)_3$, $Mn(OH)_2$, Na_2SO_3 etc. by passing air at ordinary temperature. Hence the conclusion of Spoehr[1] that neutral or feebly alkaline solution of carbohydrates are not oxidised by air is not correct.

From our experimental results with arsenious acid, it will be seen that in presence of $Fe(OH)_2$, arsenious acid is more readily oxidised than in presence of an equivalent amount of $Fe(OH)_3$ because in presence of $Fe(OH)_2$, induced oxidation of the arsenite takes place and in presence of $Fe(OH)_3$ oxidation of sodium arsenite takes place only by its reaction on $Fe(OH)_3$ and this has a very small velocity. These results are exactly in the same line as those obtained by Spoehr in the oxidation of sugars in presence of ferrous and ferric salts.

---

[1] J. Am. Chem. Soc., 46, 1494 (1924).

It will be evident that substances which are difficultly oxidised by passing air can be usually more readily oxidised in presence of reducing agents than in presence of a feeble oxidising agent like ferric salt or cupric salt.

Reinders and Vles[1] have shown that cupric salts accelerate the oxidation of arsenites by air but we are of the opinion that cuprous salts acting as inductors will accelerate the reaction better than cupric salts as shown by our experimental results.

Titoff[2] and others have shown that cupric salts act as marked accelerators in the oxidation of sulphites. Similarly ferric salts, cupric salts are known to accelerate the reactions between $K_2S_2O_8$ and KI, naphthalene and H_2SO_4 etc. We are of the opinion that in all such cases feeble oxidising agents like cupric salts, ferric salts etc., react on the reducing agents very rapidly and are themselves reduced to the ferrous or cuprous salts which, in their turn, are oxidised by air or other oxidising agents. Consequently we believe that usually weak oxidising agents ought to act as accelerators in the oxidation of substances which are readily oxidised. Moreover $Ni(OH)_2$, $Co(OH)_2$, $Mn(OH)_2$ etc. can accelerate the oxidation of Na_2SO_3 by air. This is due to the fact that when a molecule of Na_2SO_3 is oxidised to Na_2SO_4, a molecule of the hydroxides is also oxidised due to induction and this higher oxide readily reacts on the sulphite and readily passes into the lower oxide which in its turn again passes into higher oxide and this process goes on.

In a previous paper[3] it has been observed that in the dark the reaction between potassium oxalate and $HgCl_2$ is much slower than the reaction between $HgCl_2$ and sodium formate under identical conditions. Consequently as far as $HgCl_2$ is concerned, the formate ion is a better reducing agent than the oxalate ion. Moreover in the same paper it was shown that the reaction between oxalic acid and chromic acid is much quicker than that between chromic acid and formic acid under identical conditions. This shows that undissociated oxalic acid is a better reducing agent than undissociated formic acid towards chromic acid. Exactly similar results is obtained with oxalic acid and formic acid towards $KMnO_4$. It is well known that when $KMnO_4$ reacts with formic acid, MnO_2 is precipitated whilst with oxalic acid, manganous salts are produced. We have also proved that manganous salts act as marked accelerators in the oxidation of oxalic acid by $KMnO_4$ or $H_2Cr_2O_7$, whilst manganous salts act as marked retarders in the oxidation of formic acid by $KMnO_4$, or $H_2Cr_2O_7$. This is most likely due to the fact that in presence of $KMnO_4$ or $H_2Cr_2O_7$ the manganese ions are converted into $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which react very readily on oxalic acid producing $Mn^{\cdot\cdot}$ ions again, whilst the $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which are formed by the reaction between manganous salts and $KMnO_4$ or $H_2Cr_2O_7$ cannot at all react with formic acid. Consequently a part of the $KMnO_4$ or $H_2Cr_2O_7$ is taken up by the manganous salts in their conversion to $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions which are practically useless towards the oxidation of formic acid and it appears, therefore, that a part of the $MKnO_4$ or $H_2Cr_2O_7$ is lost as far as the oxidation of formic acid is concerned due to the presence of the $Mn^{\cdot\cdot}$ ions; that is why manganous salts behave as negative catalysts in the oxidation of formic acid by $H_2Cr_2O_7$ or $KMnO_4$. On the other hand, $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions can react very readily with oxalic acid. Moreover the formation of $Mn^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot\cdot\cdot}$ ions by the reaction between $KMnO_4$ or $H_2Cr_2O_7$ and $Mn^{\cdot\cdot}$ ions is a very rapid process, because we know that MnO_2 is very readily precipitated by the interaction of manganous salts and $KMnO_4$. Thus the positive catalytic action of manganous salts on the reaction between oxalic acid and $KMnO_4$ or $H_2Cr_2O_7$ is readily explained.

---

[1] Rec. Trav. chim., **44**, 29 (1925).

[2] Titoff: Z. physik. Chem., **45**, 645 (1903).

[3] Dhar: J. Chem. Soc., **111**, 707 (1917).

The retardation in the oxidation of sodium sulphite by air in presence of alkali is probably due to the decrease in the concentration of sulphite ions due to the common sodium ions. Moreover the solubility of oxygen in water is likely to be less in presence of strong alkali.

Summary and Conclusion

1. When a stream of air is allowed to pass slowly through solutions of carbohydrates like maltose, arabinose, laevulose, galactose, glucose, lactose, cane sugar and starch in presence of ferrous hydroxide or sodium sulphite, oxidation of the carbohydrates takes place at the ordinary temperature.
2. Uric acid is oxidised by air in presence of alkali, sodium sulphite, ferrous hydroxide, cupric hydroxide, manganous hydroxide, chromous hydroxide, cerous hydroxide, cuprous hydroxide, cobaltous and nickelous hydroxide.
3. Sodium arsenite can be oxidised in presence of the above hydroxides.
4. Sodium nitrite has been oxidised by air in presence of ferrous hydroxide only.
5. Explanation of several catalytic oxidations has been advanced.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
January 16, 1926.

ELECTROKINETIC BEHAVIOUR AND ELECTRODE POTENTIAL

BY F. L. USHER

The double layer of ions generally assumed to be responsible for electrokinetic effects is similar, electrically, to that implied in the generally accepted theory of electrode potential. The question of their identity is one of considerable importance. This identity was assumed by Billiter[1] who formed an estimate of single electrode potential by determining the concentration of a particular ion required to annul electrokinetic effects, the normal potential being then calculated by means of Nernst's formula. The value so obtained differed by about half a volt from that based on experiments with a dropping mercury electrode and on the electrocapillary behaviour of the same metal. The results obtained by Haber and Klemensiewicz[2] and by Freundlich and Rona[3] have on the other hand furnished conclusive proof that, at least in the case of the glass surfaces studied by them, electrode potential and electrokinetic potential are distinct. In view of the apparently decisive nature of these later results, it is interesting to find that the identity of the two potentials has quite recently been again assumed[4] in the case of metals.

If the outer member of the double layer which is the seat of electrode potential is mobile, this and the inner member—and with them the surfaces to which they are respectively attached—must, when exposed to a suitably oriented electric field, undergo a relative displacement which will give rise to electrokinetic effects of the kind generally observed. If, on the other hand, the two members of the "Nernst" double layer are not relatively displaced by the tangential component of an applied electric force, the theory of electrokinetic phenomena due to Helmholtz is by implication deprived of its fundamental assumption, unless we postulate the existence of a second superposed double layer similar to the first in every respect but that of the relative mobility of its components.

The former alternative, if true, requires a modification of a somewhat revolutionary character in the current theory of electrode potential, inasmuch as the magnitude and even the sign of the charge on the mobile surface of a metal can be changed by the addition of small quantities of electrolytes that can have little if any influence on the concentration of the metal ion generally regarded as the sole determinant of electrode potential. It raises the question whether electrode potential may in fact be due primarily to an electric charge imparted by an adsorbed layer of ions of any kind, rather than to the existence in the liquid of ions of one particular kind. In order to obtain information which might help in deciding between the two views just referred to, experiments on the influence of some uni-univalent electrolytes on the electrode potential of mercury have been carried out, side by side with electrocapillary measurements. The influence of a single electrolyte, potassium chloride, on the electrokinetic properties of a positively and a negatively charged surface has also been examined.

---

[1] Z. Elektrochem., **8**, 638 (1902); **15**, 439 (1909).

[2] Z. physik. Chem., **67**, 385 (1909).

[3] Sitzungsber. Akad. Wiss. Berlin, **20**, 397 (1920).

[4] Garrison: J. Am. Chem. Soc., **45**, 37 (1923).

Experimental

The mercury used was first purified by spraying through a long column of acidified mercurous nitrate solution, and was afterwards distilled slowly in a vacuum. The electrolytes examined were lithium, potassium, and ammonium chlorides, hydrochloric acid, potassium hydroxide, and sodium citrate, in four degrees of dilution from millinormal to normal. Two of these substances, ammonium chloride and sodium citrate, are capable of holding finely divided mercury in a stable suspension, positively charged in the first case, negatively in the second. The combination whose E. M. F. was measured consisted of the mercury in contact with the solution under examination, which was connected through a saturated solution of potassium chloride with a decinormal calomel electrode, this pair of elements being connected in series with a standard cadmium cell through a reversing key. Half the difference between the readings obtained before and after the poles of the first-named pair of elements were reversed was taken as its E. M. F. The values at 25° are given in Table I.

TABLE I

	Potential against N/10 calomel electrode at 25°					
Dilution	LiCl	KCl	NH_4Cl	HCl	KOH	Na Citrate
N/1000	0.067	0.068	0.065	0.111	−0.104	0.125
N/100	0.052	0.051	0.049	0.049	−0.150	0.073
N/10	0.003	0.002	−0.003	−0.001	−0 182	0.008
N	−0.062	−0.068	−0.063	−0.068	−0.227	−0.014

Four of the electrolytes, potassium chloride, ammonium chloride, potassium hydroxide, and sodium citrate, were then made up with a dilute solution of hydrazine hydrate (0.038 *N*) instead of water, and the results are given in Table II.

TABLE II

	Potential against N/10 calomel electrode at 25°			
Dilution	KCl	NH_4Cl	KOH	Na Citrate
N/1000	−0.57	−0.53	−0.48	−0.55
N/100	−0.56	−0.50	−0.57	−0.55
N/10	−0.47	−0.44	−0.70	−0.56
N	−0.45	−0.27	−0.72	−0.55

The electrocapillary curves were determined in the usual manner, and the same solutions (omitting lithium chloride) were used as for the measurements of electrode potential. The voltage corresponding to the maximum interfacial tension was obtained by adjusting the applied voltage in steps of 0.01

volt; otherwise readings were taken only for steps of 0.1 volt. The potential corresponding to the maximum tension (considered to be the natural potential) is given to the nearest hundredth of a volt, and the error is probably not greater than this for the normal and decinormal solutions, but the uncertainty in the case of the millinormal solutions may amount to as much as 0.05 volt, owing to the flatness of the curve near the maximum at great dilutions. It is unnecessary to give the full experimental readings. These were plotted, and from the smoothed curves the constants of the ascending branch of the parabolas were calculated by means of the formula $\gamma = \gamma_{max} - \frac{1}{2}CE^2$, C and E being respectively the capacity and potential of the double layer in electrostatic units. In Table III the natural potentials are given, for convenience, in volts, the other electrical quantities in electrostatic units.

TABLE III

Solution	Natural potential (volts)	Maximum interfacial tension (dynes per cm.)	Capacity (e. s. unit $\times 10^{-7}$)	Surface density of charge (e. s. unit $\times 10^{-7}$)	Thickness of double layer (cm. $\times 10^{7}$)
KCl					
$N/1000$	0.75	420	2.34	5.9	2.7
$N/100$	0.70	426	2.32	5.4	2.7
$N/10$	0.62	426	2.32	4.8	2.7
N	0.53	420	2.32	4.1	2.7
NH_4Cl					
$N/1000$	0.75	414	1.66	4.2	3.8
$N/10$	0.63	426	2.58	5.4	2.5
N	0.55	423	3.36	7.1	1.9
HCl					
$N/100$	0.63	426	2.2	4.6	2.9
$N/10$	0.60	427	2.92	5.8	2.2
N	0.56	419	3.8	7.1	1.7
KOH					
$N/1000$	0.60	421	1.70	3.4	3.8
$N/100$	0.59	424	1.36	2.7	4.7
$N/10$	0.54	417	1.30	2.3	5.0
N	0.40	413	1.32	1.8	4.8
Na Cit.					
$N/100$	0.67	423	2.44	5.2	2.6
$N/10$	0.57	425	2.94	5.6	2.2
N	0.42	414	4.2	5.9	1.5
N-KCl with hydrazine	0.42	434	2.7	3.8	2.4

In Table III, the interfacial tensions have been taken as proportional to the corrected measured heights of the mercury column, the factor of proportionality being obtained by measuring, in the same apparatus, the height of the column supported by solutions of hydrochloric acid of the strengths used by Lenkewitz[1] in his determinations of this constant.

The following electro-osmotic experiments were carried out in order to ascertain (1) whether potassium chloride brings about an initial increase of charge in the case of a positive as well as a negative surface, and (2) whether this effect persists in the presence of a strongly adsorbed ion having a charge of the same sign as the surface. An "alundum" thimble (made for use in an extraction apparatus) was used as the diaphragm. It was soaked for some days in concentrated hydrochloric acid in order to remove any soluble mineral matter, and then thoroughly washed with water until the electro-osmotic flow became constant. This diaphragm was negative to water, and when required as a positive diaphragm was soaked first in dilute alum solution, then in ammonia, and finally washed as before. It was found convenient to measure the pressure balancing the electro-osmotic force in the case of the negative diaphragm, and the rate of flow of liquid in the case of the positive. The inner electrode was a straight piece of stout platinum wire sealed into a glass tube at its upper end, this tube passing through a hole in the centre of a rubber stopper which fitted tightly into the top of the thimble. The glass tube was provided with distance pieces which ensured the replacement of the electrode in a central position. The outer electrode was a long spiral of platinum wire wound on a glass frame which fitted closely into the containing vessel. The thimble was replaced after each refilling in the same relative position with respect to the outer electrode by taking cross bearings on two fixed pairs of uprights.

Measurements were made of the effect of potassium chloride when the negative diaphragm was in contact with (1) water, (2) 0.2-millinormal NaOH, and (3) millinormal NaOH; and when the positive diaphragm was in contact with (1) water and (2) 0.5-millinormal $Al_2(SO_4)_3$. The potential difference between the electrodes was 22 volts, which produced an easily measurable effect, but even at this voltage the measurements at concentrations greater than six milli-equivalents per litre were unreliable. The potassium chloride solution was made up with the appropriate liquid, water, NaOH, or $Al_2(SO_4)_3$, so that the only variable concentration in any particular experiment was that of the potassium chloride. In Table IV the figures given under "relative surface charge" are proportional to the readings of pressure or rate of flow of liquid. They denote the surface density of the uncompensated electric charge, and are comparable within each series, although the numbers given in Series I are not comparable with those in Series II. In all cases the figures given represent the mean of two or more readings. The error depends on the concentration of the electrolyte. In the pressure measurements the maximum disagreement varied from three per cent. below a concentration of one milliequivalent per litre to ten per cent. at higher concentrations; and in the measurements of electro-osmotic flow the corresponding errors were roughly twice as great.

---

[1] "Untersuchung über Kapillarität". Münster, 1904.

TABLE IV

Influence of potassium chloride on electro-osmotic effect

SERIES I. Diaphragm negative.

Milli-equivs. KCl per litre	Relative surface charge in		
	water	N/5000 NaOH	N/1000 NaOH
0	1	2.71	2.22
0.1	1.39	2.12	1.56
0.2	1.58	2.58	2.46
0.3	1.44	2.48	2.39
0.4	1.66	—	2.66
0.5	1.73	2.13	2.37
0.6	2.02	—	—
0.7	1.93	—	2.44
0.75	—	2.66	—
0.8	1.83	—	—
0.9	1.95	—	—
1.0	1.88	2.54	2.12
1.5	1.97	—	—
2.0	2.05	1.93	2.20
3.0	2.02	2.17	1.68
4.0	2.05	1.66	2.10
5.0	—	2.13	1.80
6.0	2.17		
8.0	1.95		
10.0	1.39		

SERIES II. Diaphragm positive.

Milli-equivs. KCl per litre	Relative surface charge in	
	water	N/2000 $Al_2(SO_4)_3$
0	1	2.64
0.1	1.84	2.16
0.2	2.20	2.04
0.4	2.80	1.80
0.6	2.54	1.96
0.8	2.92	2.32
1.0	2.68	2.24
1.5	—	2.28
2.0	2.48	2.08
3.0	—	1.60
4.0	1.56	0.84
6.0	0.56	—

Fig. 1 shows the relative surface densities of the charge plotted against the concentrations of KCl so as to indicate the general sense of the effects in the case of the negative diaphragm, and Fig. 2 shows the initial portions of the curves with the concentration scale magnified. Figs. 3 and 4 show the corresponding curves for the positive diaphragm.

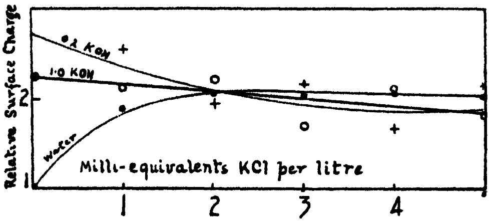


FIG. 1

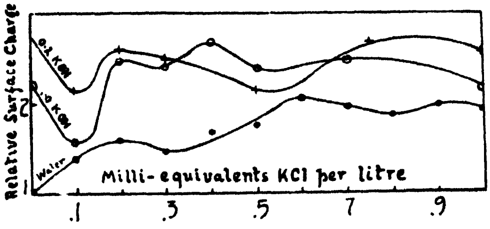


FIG. 2

Discussion of Results

If, as it will be assumed, the liquid contact potentials between the solutions examined and the decinormal potassium chloride used in the reference electrode were eliminated by the use of the salt bridge, the measured potentials must be the algebraic sum of the potential differences across all double layers situated at the interface of the mercury and the solutions used, *minus* the sum of the corresponding potentials at the mercury-solution interface in the reference electrode. The value of the latter is not known with certainty, but is in any case constant, so that, by subtracting some constant quantity from the experimental values, it might be expected that figures would be obtained bearing some relation to the electrokinetic behaviour of mercury in the corresponding solutions. It is quite evident that no such constant quantity can be chosen so as to reveal even a suggestion of parallelism between the transversely measured potential and the electrokinetic behaviour. Finely divided mercury is known to move towards the cathode in dilute solutions of ammonium chloride, towards the anode in dilute sodium citrate, and not at all in dilute potassium chloride. On comparing the experimental values for these three salts in centinormal and millinormal solution, it is seen that, while there is very little difference between the values for potassium and ammonium chlorides, the mercury is more positive in sodium citrate than in either of the others. Again, it is more negative in solutions of potassium hydroxide, although no stable suspension can be obtained in them. There is, in fact, a complete absence of any correlation between the transversely measured potential and the electrokinetic behaviour.

One or two points of interest emerge, however, from a consideration of the figures. It may be noticed that the potentials of mercury in decinormal solutions of the chlorides examined are substantially the same as those of the mercury in the decinormal calomel electrode, and that the influence of change of concentration is, at least qualitatively, the same as in the case of a calomel electrode. This striking similarity of behaviour is not likely to be accidental, and there can be little doubt that the potential of mercury is in both cases determined by the same factor, namely, the activity of the mercurous ions in the liquid. But it was found that mercury could not be detected (by means of hydrogen sulphide) in any of the solutions used, although of course it is easily recognisable in the solution used in the calomel electrode. It would appear therefore that at great dilutions the concentration of mercurous ions at the mercury surface is almost independent of the bulk concentration, and

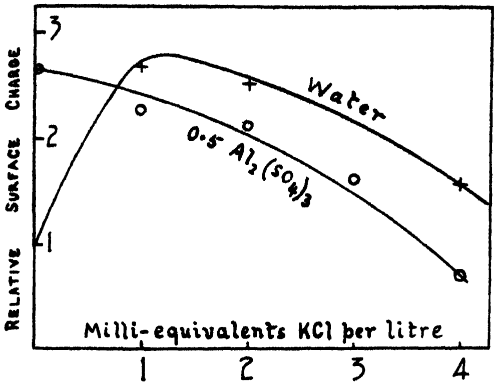


FIG. 3

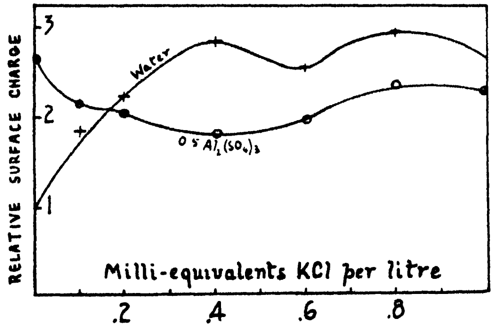


FIG. 4

it is reasonable to infer that in all the solutions examined sufficient mercurous ions were formed by chemical action to provide a layer covering the mercury surface. Assuming the chemical action to be due to dissolved oxygen, one finds that only about 2×10^{-8} gram of oxygen would be required to produce 1 sq. cm. of a unimolecular film of mercurous ions. It is obviously impracticable to carry out experiments in which so small a quantity of oxygen could be excluded with certainty, and some measurements were therefore made in presence of hydrazine hydrate which, provided the solution is alkaline, reduces mercury compounds even at very great dilution: mercuric sulphide was indeed the only compound examined which resisted reduction. As is evident from Table II, the effect of the hydrazine, which was present in the same concentration throughout, is remarkable. The potentials are given only to the nearest centivolt, since they were not reproducible with greater accuracy, presumably because the electrodes under these conditions are practically irreversible. It will be seen that the effect of changing concentration of the electrolyte is now in the opposite sense, the potential of the mercury becoming more positive with increasing concentration, except with sodium citrate and potassium hydroxide, an observation which suggests that it is no longer determined by mercurous ions. It will also be noticed that there is still little to suggest a connection between the measured potentials and the mobility of mercury in the corresponding solutions.

Electrocapillary measurements. The constants given in Table III are those relating to the parabola $\gamma = \gamma_{max} - \frac{1}{2}CE^2$, and were obtained by drawing the curves with the maximum interfacial tension at $E = 0$. The "natural" potentials deduced from the electrocapillary experiments show divergencies from those reckoned from the measurements of electrode potential (taking the absolute potential of the decinormal calomel electrode as 0.61 volt) which are difficult to explain quantitatively in the present state of our knowledge, but the general results are similar. The figures are recorded here chiefly because we can deduce from them some particulars regarding the properties of the double layer responsible for the natural potential. It has been stated[1] that the relation between the interfacial tension and potential should be expressed by the equation $\gamma = \gamma_{max} - CE^2$, following a suggestion made by Krüger and Krumreich[2] that the variation of interfacial tension with surface charge should be doubled in order to include the effect of both sides of the double layer. This suggestion was originally put forward to explain a discrepancy between results obtained by two different experimental methods, but it appears to be contrary to theoretical requirements as deduced, for example, by applying the principle of Virtual Work. Thus, in a double layer of unit area, forming a condenser of capacity C, let a small positive charge, δQ, be transferred from the positive to the negative side. The work terms involved are $E\delta Q + \partial y/\partial Q \,.\, \delta Q$, which, since the system is in equilibrium and the change takes place at constant temperature and volume, must be equated to zero.

---

[1] Freundlich: "Kapillarchemie", 395 (1922).

[2] Krüger and Krumreich: Z. Elektrochem., 19, 620 (1913).

Hence $\partial y/\partial Q = -E$, or $\partial y/\partial E = -CE$. If the capacity is assumed to be constant we obtain on integrating,

$$\gamma = \gamma_{\max} - \tfrac{1}{2}CE^2,$$

without having made any assumption regarding the effectiveness of one or both sides of the double layer.

The capacity being thus determined from the electrocapillary curves, it is easy to calculate the charge per unit surface, and also the thickness of the double layer. These quantities are given in Table III, the thickness of the double layer being calculated on the assumption that the dielectric constant of the medium separating its two components is 80: the values obtained by taking it as unity are so much smaller (about 3×10^{-9} cm.) than the normal spacing of atoms that the former alternative seems preferable.

It is interesting to find that, although potassium chloride is probably the only one of the electrolytes used which behaves in an approximately normal manner (in not giving rise to any adsorption of its ions at the electrocapillary maximum), the values for the charge per unit surface and for the thickness of the double layer are all of the same order of magnitude. Thus the surface charge (positive) in ammonium chloride is about 5×10^4 c. s. units, and in sodium citrate it is practically the same, and still positive; yet in regard to its electrokinetic behaviour mercury is positive in the former but negative in the latter.

Effect of potassium chloride on electrokinetic charge. The curves in Figs. 1 and 3 indicate that the general effect of potassium chloride on the electrokinetic potential of a negatively charged surface, when no other electrolyte is present, is first to increase the negative charge and afterwards to reduce it; while with a positively charged surface under similar conditions the effect is first to increase the positive charge and then to reduce it. When another electrolyte of a kind which strongly enhances the natural charge is also present, the tendency of the potassium chloride to increase it is much less marked. While these statements represent the general tendency of the electrokinetic potential under the conditions named, a closer examination of the figures for very small concentrations reveals a series of subsidiary maxima and minima in the curve, which can hardly be attributed to experimental error: the initial portions of the curves in every case have a sinuous form. It is to be noticed that the first effect of the potassium chloride is to increase the natural charge, whether positive or negative, unless this has already been enhanced by the previous addition of a suitable electrolyte.

It has been pointed out elsewhere[1] that an initial increase of surface charge may be expected to occur when the free ions produced by the dissociation of surface molecules are replaced by others which have less tendency to combine with the residual sessile ions. Thus, the addition of an alkali metal salt in sufficiently great dilution in the case of a surface giving rise to free hydrogen ions should always cause such an increase, and this is confirmed by the data so far available. But there are instances in which this explanation is inapplicable.[1] Kruyt, in measuring the electrokinetic effect at a glass-water interface, has found that an initial increase of charge is produced not only by potassium chloride, but also by hydrochloric acid and by barium chloride. This behaviour can hardly be covered by the considerations just referred to, and may best be explained by assuming an adsorption of chloride ions at the surface of the glass. A similar assumption seems necessary to explain the results shown in Table IV and Figs. 1-4. It is evident that in these experiments two processes are at work whose effects are opposed. In the case of the "alundum" diaphragm, whose natural charge in water is negative, the potassium chloride added furnishes chloride ions which are adsorbed and thus increase the negative charge of the surface, further addition of the electrolyte then acting in the normal manner and recuding the dissociation of the surface molecules. These two effects predominate alternately, and would presumably continue to do so until the surface was fully occupied by the negative ions of dissociated and undissociated molecules—a stage which cannot be reached experimentally on account of difficulties of measurement. With an alumina diaphragm whose natural charge is positive, the cations of the electrolyte are adsorbed, and the further course of events is then much the same as before. This view of what occurs is supported by the observation that when in the first case a strongly adsorbed anion, in the second a strongly adsorbed cation, is initially present, the increase of the initial charge is either much smaller, or does not occur.

---

[1] Trans. Faraday Soc., **21**, Part 2 (1925).

Summary

1. Measurements of the contact potential and of the electrocapillary behaviour of mercury in solutions of different uni-univalent electrolytes indicate the absence of any direct connection between electrode potential and electrokinetic behaviour in the case of this metal.

2. A comparison of the potentials of mercury in solutions of chlorides with and without the addition of hydrazine, indicates that whenever the metal is brought into contact with such solutions, chemical action results in the production of mercurous ions which are present at the interface in nearly the same degree of concentration as if the solutions had previously been saturated with calomel.

3. Electro-osmotic experiments on the influence of potassium chloride on the surface charge of a diaphragm point to an initial adsorption of that ion which enhances the original charge, this effect being greatly reduced when a strongly adsorbed ion bearing the same charge as the surface is present.

Department of Chemistry,
University of Mysore,
Bangalore.

---

[1] Kolloid-Z., **22**, 81 (1918).

MECHANISM OF THE CATALYTIC DEHYDRATION OF METHANOL AND SOME PROPERTIES OF THE HYDROUS ALUMINIUM OXIDE CATALYST*

BY H. C. HOWARD, JR.

Our present knowledge in regard to the mechanism of catalysis can be accurately classified under three general heads: (1) those cases in which intermediate compound formation has been definitely proven; (2) those cases in which absence of compound formation has been demonstrated; and (3) a type of catalytic reaction in which the matter of the formation of an intermediate chemical compound is still controversial, or merely a matter of definition. On this question of intermediate compound formation in catalysis, Sabatier states that "the idea of a temporary, unstable, intermediate compound has been the beacon light that has guided all my work on catalysis." Consequently, he explains such a catalytic reaction as the dehydration of an alcohol over hydrous aluminium oxide, by assuming a mechanism analogous to that assigned to the Williamson reaction. Aluminium is an amphoteric element, so that its compounds will possess both basic and acidic properties, and the analogy of the role played by the alumina catalyst, in the dehydration of an alcohol, to that of the sulfuric acid in the Williamson reaction, is most clearly brought out if the reaction over the alumina catalyst is pictured as taking place by the addition of a mol of the alcohol to the acidic form of the aluminium hydroxide, H_3AlO_3, or its partial dehydration product, $HAlO_2$, as shown in the following equations:

$$CH_3OH + HAlO_2 \longrightarrow CH_3AlO_2 + HOH$$
$$CH_3AlO_2 + CH_3OH \longrightarrow (CH_3)_2O + HAlO_2$$

Such a mechanism lays emphasis upon the acid properties of the oxide, and the following facts indicate that such properties are of importance.

(1) Only amphoteric or acidic oxides have been shown to be capable of acting as dehydration catalysts in such a reaction; that is, no exclusively basic oxide has been shown to function in this manner.

(2) The effectiveness of a given oxide as a dehydration catalyst appears in many cases to be related to its "acidity." The compounds formed by the hydration of such strongly acidic oxides as SO_3 and P_2O_5 are excellent catalysts of dehydration. The hydrous forms of weakly acidic oxides such as Al_2O_3 are fairly active, while those of the very weakly acidic oxides such as Fe_2O_3 exhibit catalytic dehydrating power to only a very limited degree, indeed.

(3) Those methods of preparation which would be expected to yield a catalyst in which the acidic form of the hydrated oxide predominated, are, in general, the methods which furnish the most active dehydration catalysts.

---

*Contribution from the Chemical Laboratory, University of Missouri.

(4) Chariou[1] has shown that adsorbed lime on an alumina catalyst decreases very markedly the activity of such a catalyst in the dehydration of ethyl alcohol to ether, and Taylor[2] has pointed out that Adkins' data show the adverse effect of ammonia in catalytic dehydration.

Adkins[3] questions the formation of a compound or compounds between the alcohol and the catalyst because such an hypothesis necessitates the assumption of two different types of compounds in the case of oxides which are capable of inducing two different types of catalysis. In every case it will be noted that it is an amphoteric oxide which is capable of exercising this dual function. Hence it appears possible to the writer that in the case of oxides of the amphoteric elements we *do* have two or more forms present, the relative amount of each form being determined by the method of preparation.

It is possible to make a partial test, at least, of Sabatier's hypothesis, by an application of the Phase Rule, and in this investigation such an application has been made.

If, in a system consisting of methyl alcohol and hydrous aluminium oxide, the alcohol forms a compound with the oxide and the properties of this compound are such as to render it a separate phase, we will be dealing with a three-phase, two-component system, a system having one degree of freedom. If, on the other hand, no compound is formed, or a compound which dissolves in the alumina to form a single phase, then we will have a two-phase, two-component system and two degrees of freedom. The methods used in distinguishing between these two types of system are discussed in the following paragraphs.

Type A. Assume a system such as $C_nH_{2n}AlO_2+HAlO_2$ (in which the compound $C_nH_{2n}AlO_2$ constitutes a separate phase), in an atmosphere of an inert gas, such as nitrogen,[4] and assume the total pressure on the system to be 760 mm. In such a system, at any definite temperature, there will be a certain equilibrium concentration of $C_nH_{2n}AlO_2+HAlO_2$ and C_nH_{2n}. If the temperature be raised, more $C_nH_{2n}AlO_2$ will dissociate, with the formation of $HAlO_2$ and C_nH_{2n}, and the pressure in the system will tend to increase, but up to a certain temperature the total pressure in the system can be held at 760 mm. (the initially chosen value) by allowing the C_nH_{2n} and the nitrogen to expand, and more $C_nH_{2n}AlO_2$ to dissociate, since by this means the partial pressure of C_nH_{2n} in the gas phase can be increased. Ultimately, however, if the temperature is increased sufficiently, the dissociation pressure of the compound $C_nH_{2n}AlO_2$ will become greater than the possible attainable partial pressure of C_nH_{2n} in the gas phase, (in this case 760 mm. will be the limiting value) and dissociation will then continue as long as any of the $C_nH_{2n}AlO_2$ phase remains. In this type of system the vapor pressure is *not* a function of the concentration.

---

[1] Compt. rend. **180**, 213 (1925).

[2] J. Phys. Chem. **30**, 167 (1926).

[3] J. Phys. Chem., **30**, 167 (1926).

[4] The use of nitrogen introduces another component and another degree of freedom in each case, but the method of distinguishing between the two types of system is still valid. The second system still has one more degree of freedom than the first.

Type B. Assume a system similar in all respects to that described under Type A, except that the alcohol either does not react to form a compound, or if it does form a compound, the latter does not exist as separate phase. In this case it will be possible to maintain an equilibrium at any chosen pressure and temperature, merely by allowing the products of the dissociation to expand, by increasing the volume of the system. In other words, with this type of system there is no temperature at which dissociation is continuous. In this case the dissociation pressure *is* a function of the concentration.

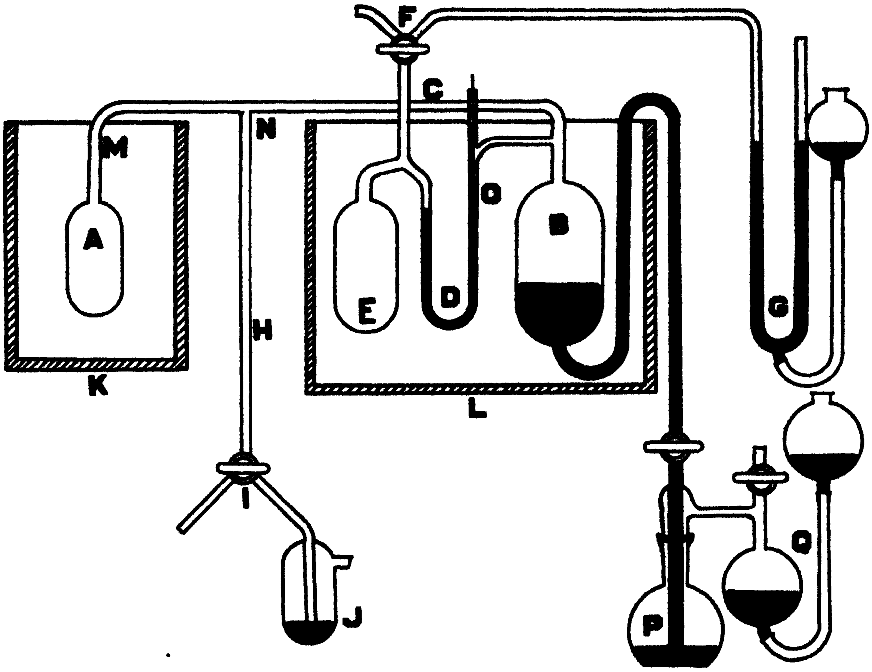


FIG. 1

Experimental

The methyl alcohol used in this work was supplied by a large manufacturer of dimethyl aniline. It gave negative tests for aldehydes and ketones and boiled 64.40°-64.55°C. at 747 mm. (Bureau of Standards certified thermometer). It was dried in the usual manner over calcium oxide. The alumina catalysts were prepared according to the directions of Sabatier, by precipitating a solution of C. P. aluminium nitrate with a slight excess of ammonium hydroxide, washing thoroughly and drying at 300°C. The dried material was ground and screened and the particles passing a U. S. Standard screen

No. 8, and retained on a No. 16, were employed in this work. This catalytic material contained about 15% water, determined by ignition at 1000°C.

The nitrogen was prepared in the usual manner from sodium nitrite and ammonium chloride. Carbon dioxide and oxides of nitrogen were removed by sodium hydroxide, and oxygen by hot copper. It was washed with water and finally dried over phosphorous pentoxide.

The apparatus used in this study is shown in Fig. 1. It consisted essentially of a bulb "A", communicating through a capillary "C" with a weighing burette "B". The burette communicated with a small mannometer "D" and the other leg of this manometer opened into a compensating bulb "E". The latter could be connected to vacuum or pressure, or to the large constant volume manometer "G", by means of the stop-cock "F". The vertical capillary tube "H" communicated, through the three-way cock "I", either to vacuum or pressure (through the mercury trap "J") or the supply of nitrogen and methyl alcohol vapor. The baths "K" and "L" were electrically heated and fitted with automatic temperature controls. "K" was a bath of potassium acid phosphate and phosphoric acid and could be maintained at any temperature desired between 180° and 400°C. "L" was a glycerine bath and was kept at 100°C. Only about 10 cm. of the communicating capillary "C" was not immersed in either bath and this part was lagged with asbestos string.

Method of Manipulation

The bulb "A" was filled with a sample of the catalyst and sealed to the communicating capillary "C" at some point such as "M". Bath "K" was then brought into position and maintained at 180°C. Bath "L" was brought to 100°C. and the whole system evacuated through cocks "F" and "I" until the pressure fell to a few mm. The mixture of methyl alcohol vapor and the nitrogen (the nitrogen was saturated with methyl alcohol at 25°C) was then introduced through "I" until the pressure in the system was about 10 cm. less than atmospheric, air being introduced simultaneously through "F," to maintain the pressure on both sides of the mannometer "D", approximately the same. Cock "I" was now cautiously turned to communicate with the mercury trap "J", which was open to atmospheric pressure, and mercury allowed to flow up into the capillary "H", until the point "N" was reached. Stop-cock "I" was then shut off, the column of mercury in "H" effectively sealing it. The pressure in the system was now adjusted[1] (by means of the burette "B", the weighing bottle "P" and leveling bulb "Q") to some definite value, by the indicating point shown at "O".

Several weighings of the mercury and weighing bottle were made and the average recorded. The temperature was increased by increments of approximately 20°C. Time was given for the attainment of temperature equilibrium at the end of each increment, and several weighings of the weighing bottle were made at definite time intervals. Data, typical of many measurements are presented in Fig. 2 in the form of a curve. Temperatures of the catalyst bulb are plotted as ordinates and weights of the weighing bottle as abscissa. The weights of the weighing bottle, or rather the changes in weight of the weighing bottle, are evidently inversely proportional to the changes in the amount of vapor in the bulb containing the catalyst and, because of the high density of mercury, very precise measurements of volume changes in the catalyst bulb could readily be made. The time interval between readings was approximately fifteen minutes.[1]

---

[1] For a detailed description of the method of operation of this type of burette, see J. Phys. Chem. **28**, 1082-1095 (1924).

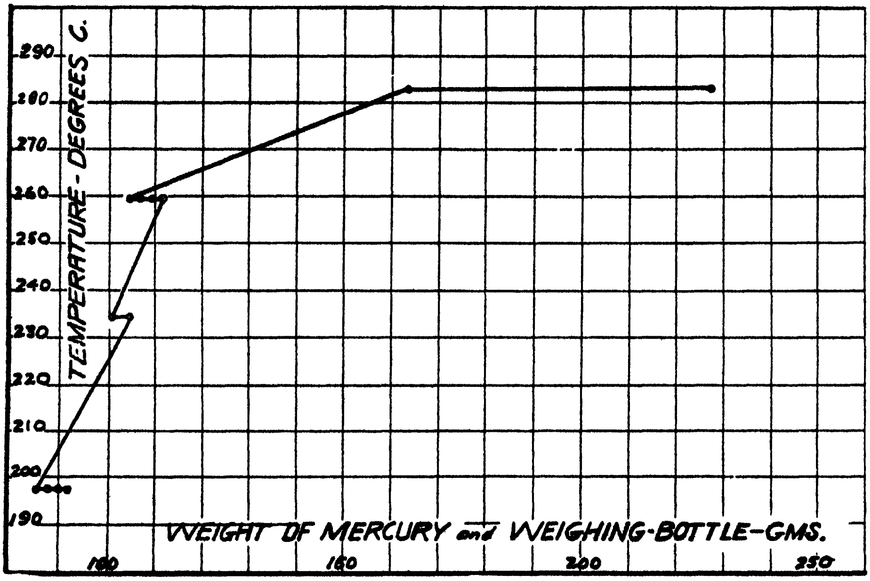


FIG. 2

At first sight it appears that this curve meets the requirements set forth under Type "A" very exactly, that is, there is a certain temperature range over which the arbitrarily chosen pressure can be maintained, merely by allowing the gas phase to expand into the burette "B", and ultimately a temperature is reached at which dissociation *appears* to be continuous A more careful analysis indicates, however, that this is a faulty conclusion. The actual change in volume over the 15 minute period at the temperature of 283°C. is approximately 0.480 cc. (the volume of 60 gm. of mercury at 100 C.). It is evident that this much vapor could evaporate from the catalyst without changing appreciably the concentration of the methyl alcohol in the alumina. That is, a flat portion to such a curve, corresponding to such a relatively small evolution of vapor, is not conclusive evidence that we have to deal with the dissociation of a separate phase of constant composition. That this latter is the correct conclusion was indicated by later experiments in which the temperature at which dissociation *appeared* to be continuous was maintained constant over a period of several hours, when a very gradual, but distinct decrease in the *rate* of vapor evolution was observed. In order to fix this point still more definitely, however, the following experiment was carried out. The catalyst and the communicating system were evacuated at 250°C until the pressure fell to a few mm. The mixture of methanol and nitrogen was then admitted until a pressure of about 550 mm. was reached. The pressure remained approximately constant at this value for about thirty minutes. Now, with the temperature constant, vapor was removed from the catalyst bulb by allowing mercury to flow out of the burette "B". The effect of this withdrawal of vapor, upon the pressure in the system, is shown in Fig. 3. It is evident from this experiment that the pressure in the system falls steadily, if any appreciable quantity of vapor is withdrawn, that is, the vapor pressure of the system *is* a function of the concentration of the methyl alcohol vapor. This system then evidently falls in the class of those described under "B" and hence we can state definitely that no compound, constituting a separate phase, is formed. Compound formation with subsequent solution in the catalyst (as in the case of the Williamson Reaction) is, of course, not excluded.

---

[1] An interesting feature of this curve is the evidence of "drift," or slow penetration of the gas phase into the catalyst, at the lower temperature. This "drift" is of about the same magnitude whether the gas phase is pure nitrogen or a mixture of nitrogen and methyl alcohol vapor. Thus it is evidently not specific in nature.

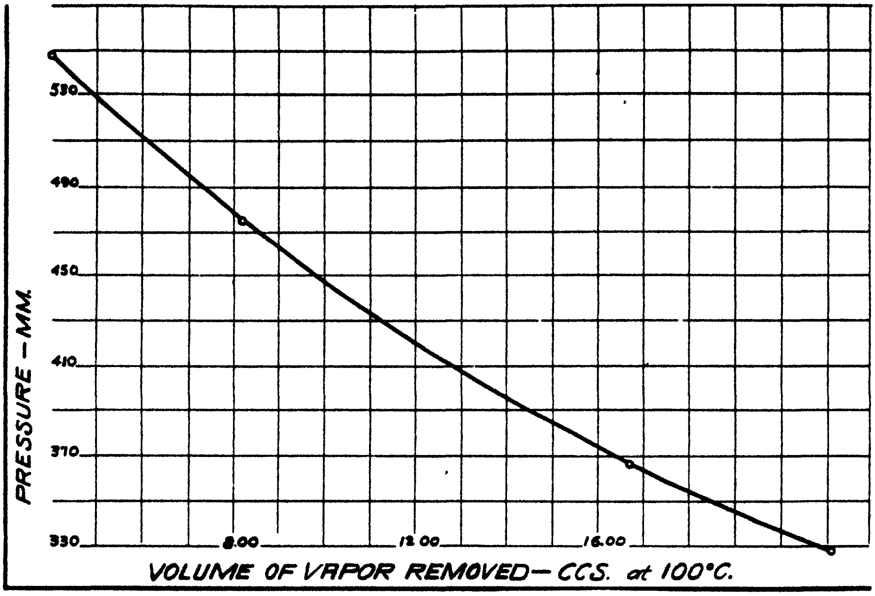


FIG. 3

In order to learn the behavior of an alumina catalyst in the presence of an inert gas alone, experiments were carried out similar in every way to those already described, except that the catalyst bulb was filled with catalyst and dry nitrogen only. To our surprise, in all cases exactly the same type of curve was obtained as that shown in Fig. 2. At first this was thought to be due to traces of CH_3OH or water remaining in the catalyst from previous experiments, so that a fresh sample of catalytic material was prepared, placed in a new bulb and sealed into position. Again, however, exactly the same type of curve was obtained. It was now observed that if several successive measurements, using dry nitrogen, and with intervening evacuation, were made upon the same sample of catalyst, that the temperature required to bring about rapid dissociation (indicated by the flat portion of the curve) became higher and higher. In many cases samples after having had vapor pressure measurements made upon them, were tested, qualitatively, for catalytic activity, and it was always observed that the catalysts showing a high "break" temperature were those requiring a high temperature to initiate the catalytic dehydration of methyl alcohol.

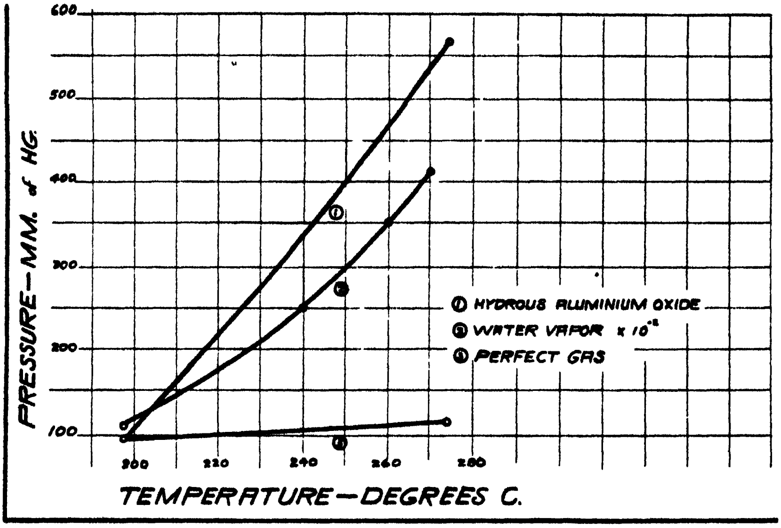


FIG. 4

The catalytic dehydration of methyl alcohol, like many other catalytic reactions is markedly affected by rather small temperature changes. Qualitative determinations with our catalytic material indicated that below 200° the reaction is very slow, while at 250° to 275° it becomes very rapid. It was thought probable that this was due to a considerable variation, with temperature, of the vapor pressure of this aluminium oxide-water complex. To test this point the following experiment was carried out. The sample was evacuated at 197°C. until the pressure in the system had fallen to 9 mm. Water vapor was now admitted until the pressure reached 98 mm. The supply of water vapor was shut off and the temperature raised to 275° C. In 27 minutes the pressure had risen to 420 mm., and at the end of 40 minutes the pressure was 568 mm., where it remained approximately constant for the next thirty minutes. The extraordinarily steep slope of the vapor pressure curve of this hydrous aluminium oxide catalyst is evident when comparison is made, as in Fig. 4, with the corresponding curve for water over the same temperature range. These data show the enormous effect of temperature on the vapor pressure of an alumina catalyst, and indicate that the temperature of catalysis is determined by the vapor pressure of this complex; when a temperature is reached such that the vapor-pressure of the complex is sufficiently great so that water can evaporate from the catalyst as fast as it is formed in the reaction, we have catalysis.

These experiments indicate that the catalytic dehydration of an alcohol over alumina takes place in some way through a water-aluminium oxide complex. Whether this be $Al(OH)_3$, or $HAlO_2$, a solid solution of water in Al_2O_3, or adsorbed water, it is impossible to say from the present data. Whatever it may be, it can be stated definitely that this complex does not constitute a separate phase.

It also appears probable that the sensitiveness to heat treatment shown by alumina catalysts, is not due, primarily, to sintering and consequent decrease of surface (change in degree of unsaturation or change in spacing) but to destruction of this complex.

It is proposed to study further the properties of alumina catalysts and to determine, if possible, the nature of this $Al_2O_3H_2O$ complex, which appears to be so essential for dehydration catalysis. In some cases alumina catalysts prepared from aluminates have been reported to be superior to those prepared in any other way. This indicates that there may be a real difference in structure between $Al(OH)_3$ prepared by precipitation by an alkali from an aluminium salt, and that produced by the acidification, or hydrolysis, of an aluminate. It seems certain at least that very different impurities would be present in the catalyst depending upon the method of preparation used.

Summary

(1) By an application of the Phase Rule to a system containing hydrous aluminium oxide and methyl alcohol, it has been shown that over the temperature range at which the oxide functions as a catalyst, no compound between the alcohol and the oxide, constituting a separate phase, is formed. The possibility of formation of a compound, with subsequent solution in the catalyst is not excluded. Hence a mechanism such as that suggested by Sabatier, analogous to the Williamson reaction, is possible.

(2) A close relation has been found between the temperature at which the evolution of water vapor from a sample of hydrous aluminium oxide be-

comes rapid, and the temperature at which catalytic dehydration of alcohol takes place over such an oxide. This relation shows the intimate connection between the presence of water in the oxide before catalysis and the process of catalysis.

(3) The magnitude of the variation of the vapor pressure of a hydrous aluminium oxide catalyst with temperature, has been determined, and the relation between this quantity, and the effect of temperature on the catalytic dehydration of an alcohol over such a catalyst has been pointed out.

Columbia, Missouri
March 24, 1926.

THE TERNARY SYSTEM: SILVER BROMIDE—POTASSIUM BROMIDE—WATER*

BY RAYMOND H. LAMBERT

Some idea of the solubility relation in a ternary system can be obtained from a study of the three pairs of binary systems, provided the data for the binary systems are available.[1] In the system instanced in the title such is the case and since the binary systems are very simple, it is possible to develop the entire surface between solid and liquid phases with only a very little extra data.

From the data in the literature[2], [3] the systems may be arranged as in Fig. 1. The dotted portions of the diagram indicate imaginary boundaries not existing at atmospheric pressure but real and nearly identical at sufficiently high pressures. An examination of the three pairs of binary mixtures leads to some interesting conclusions in regard to the ternary system.

At least two of the three pairs of binary mixtures i.e., systems, KBr-H_2O, KBr-$AgBr$, show distinct eutectic points, the former at 6.6 molar percentages of potassium bromide and the latter at 44 molar percentages potassium bromide. If in a ternary system each pair of binary systems contain only a single eutectic mixture, the phase diagram is very simple. For a non-variant system both temperature and concentration are fixed, this temperature being lower than for any other equilibrium mixture. At this point the liquid phase will be in equilibrium with three solid phases of the pure components.

Compound formation obviously makes the diagram more complex. Hellwig concluded that no compound or double salt between silver bromide and potassium bromide is found to exist in precipitates from water solution.[4] Reference will be made to this later in the paper. There is also no evidence of hydrates between either salt and water although many alkali halides do combine with water.

In this ternary system, the phase diagram may be even further simplified since any eutectic in the binary system, $AgBr$-H_2O, lies so very near the axis of the pure water component that it has never been detected. In any case it can be assumed to lie on the pure water axis. The lowest temperature at which equilibrium will exist between solid and liquid will then be at one of the other two binary eutectics, in this case, the KBr-H_2O eutectic at $-13°C$ and 6.6 molar percentages of potassium bromide.

From this assumption, one may proceed further and predict a eutectic valley leading from the $AgBr$-KBr side of the triangular diagram, figure 1, to the KBr-H_2O side exists. This valley should be a smooth path, which on a four dimensional system, temperature being represented by height, falls in temperature and composition from 290°C and 56 molar percentages of silver bromide and no water, the eutectic point of system, KBr-AgBr, at a continuous rate down to -13°C and zero silver bromide, the eutectic point of system, KBr-H_2O. For two salts in equilibrium with water, if one is extremely insoluble compared with the other, as is true with silver bromide and potassium bromide, the valley will be concave to the axis (in the triangular diagram) of the comparatively insoluble component i.e., $AgBr$-H_2O, and convex to the KBr-H_2O axis. One would expect that the degree of curvature in the eutectic valley would be greater for a pair of salts whose difference in solubility, when alone in water, is greater and that for two salts equally soluble in water, the eutectic valley would approximate to a straight line in the composition diagram.

---

* Communication No. 273 from Research Laboratory, Eastman Kodak Company.

[1] Roozeboom: "Die heterogene Gleichgewichte," 3 I.

[2] System KBr-$AgBr$. C. Sandonnini: Atti Accad. Lincei, **21** II, 197 (1912).

[3] Systems KBr-H_2O and $AgBr$-H_2O. Landolt-Börnstein Tabellen.

[4] Karl Hellwig: Z. anorg. Chem., **25**, 182 (1900).

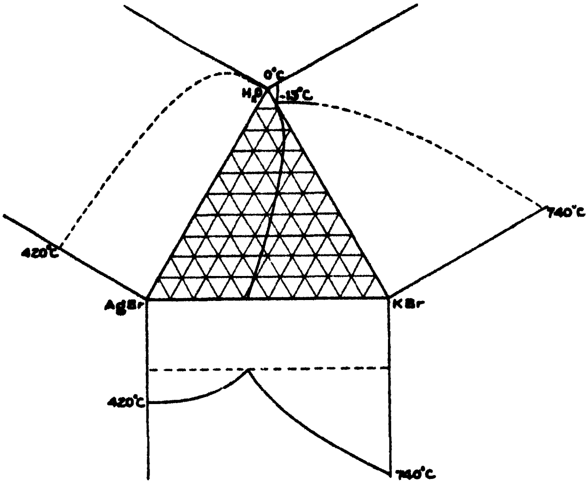


FIG. 1

Since interest lies mainly in the eutectic valley at temperatures of low vapor pressure of water, a study was made only of the solubility of silver bromide and potassium bromide co-existent in water solution in the presence of both solid salts with change of temperature up to 100°C. The method used was that suggested by Fritz Feigl[1] whereby the solution in equilibrium with solid silver bromide and potassium bromide was filtered into a porous cup which was also used as a stirrer in order to bring the system more quickly to equilibrium.

Fig. 2 is a diagrammatic sketch of the apparatus. An ordinary liquid thermostat was used. A red dye soluble in oil was added to the bath to prevent light decomposition of the silver bromide. The layer of oil prevented excessive evaporation of water from the bath at the higher temperatures. Equilibrium was obtained in about 24 hours, due to efficient stirring, after which portions of the solution were drawn off by means of a pipette which several hours before sampling had been placed in the hollow glass tube to which the porous cup was fastened. This brought the pipette to the same temperature as the bath. The special pipette made of thick walled glass tubing had a very short stem so that the liquid did not leave the porous cup until the pipette was ready to be drawn entirely from the bath.

---

[1] Fritz Feigl: Z. angew. Chem., 31, 168 (1918).

The liquid was quickly placed in tared weighing bottles and even at the highest temperatures employed little error was caused by sampling. The porous cup was alundum having the desired porosity for filtration. It was chosen from about a dozen cups.

Chemically pure potassium bromide and silver bromide were three times recrystallized together at 100°C from water solution. Samples were removed from the apparatus at ten degree intervals for increasing temperatures and at twenty degree intervals on the decreasing scale. In the latter experiments, the porous cup was not inserted until the lower temperature had been established for some time.

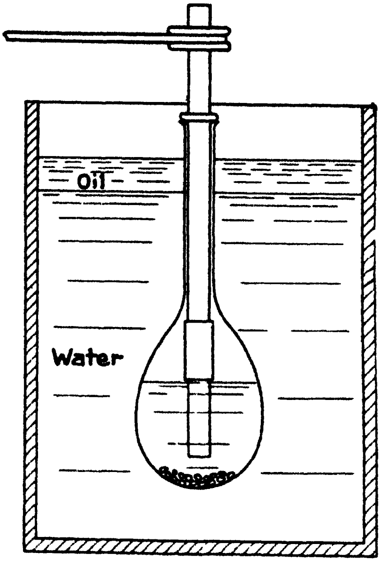


FIG. 2

TABLE I

	Per cent by Weight			Per cent by Mol.			
Temperature	AgBr	KBr	H_2O	AgBr	KBr	H_2O	Ratio KBr/AgBr
−13	0	—	—	0	6.71	93.29	∞
	1.67	39.87	58.50	0.250	9.33	90.4	37.32
30	1.636	39.54	58.82	0.242	9.21	90.54	38.06
40	2.24	40.88	56.88	0.339	9.77	89.88	28.75
	3.25	43.09	53.66	0.515	10.78	88.70	20.93
50	3.12	42.43	54.45	0.489	10.50	89.01	21.47
60	4.20	44.24	51.56	0.685	11.42	87.90	16.67
	5.80	45.48	48.72	0.990	12.26	86.75	12.38
70	5.60	45.53	48.87	0.954	12.24	86.80	12.83
80	6.72	46.91	46.38	1.192	13.12	85.69	11.01
	8.47	48.15	43.39	1.580	14.16	84.26	8.96
90	9.00	47.98	43.115	1.687	14.20	84.11	8.42
100.0	10.55	48.66	40.79	2.080	14.98	82.96	7.27

Table I contains the data both in weight and molar percentages. In Fig. 3 are plotted the weight percentages of potassium bromide and silver bromide with temperature as the abscissa. The upper curve is that for the solubility of potassium bromide alone in water, the data being taken from Landolt and Börnstein's Tabellen. It is interesting to note that 10.5 per cent by weight of silver bromide dissolves in a potassium bromide solution in equilibrium with solid potassium bromide at 100°C.

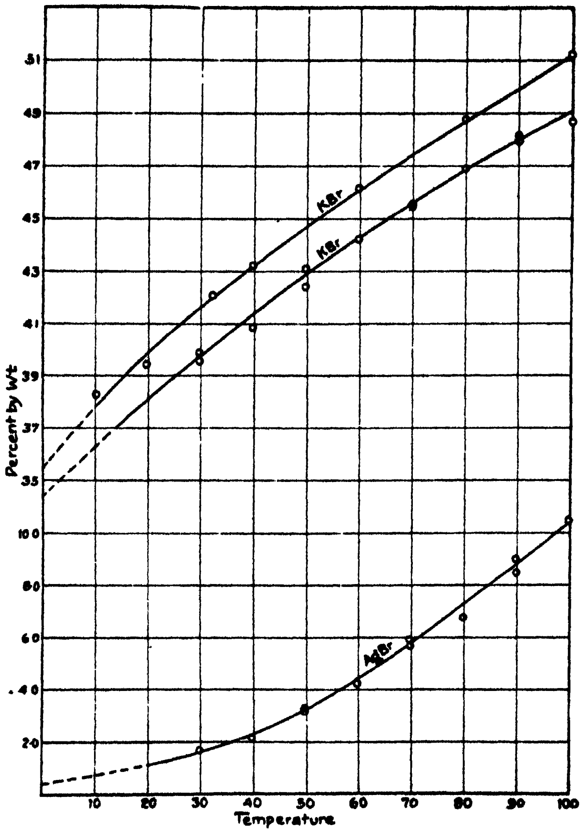


FIG. 3

The ratio of potassium bromide to silver bromide is of interest since at 290°C, Sandonnini gives the eutectic of the system, KBr-AgBr as 56 molar percentages of silver bromide. Figure 4 shows the ratio varying with temperature. The upper end of the curve should be asymptotic to the Y-axis at − 13°C

If the eutectic valley be projected on a plane for the ternary system, the result is that shown in figure 5. Horizontal lines measure molar percentages of silver bromide with zero silver bromide on the base line. Molar percentages of potassium bromide are lines parallel to the line on which molar percentages of potassium bromide is written. The third series of lines obviously corresponds to molar percentages of water. Here check points lie on a smooth curve but are not together. This would indicate an error in temperature reading. Extrapolation of the curve ends at the eutectic point of the binary mixture, KBr—H_2O, as was to be expected.

Figure 6 is an expression of the ternary system including temperature relations. The photograph is that of a plastic model and was taken expressly to show the eutectic valley. As previously stated, the system is only stable

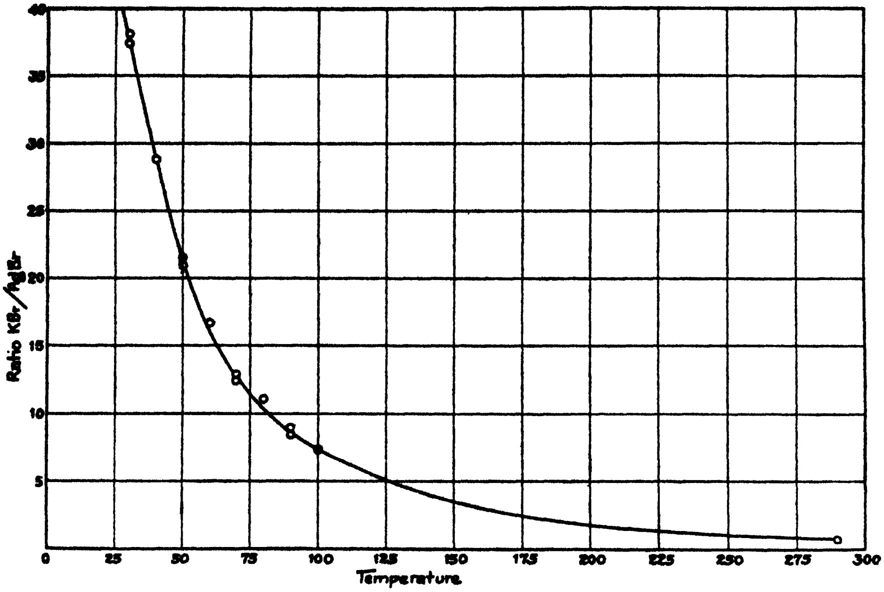


FIG. 4

for pressures greater than atmospheric since water should boil away at the high temperatures. Below 100°C, however, the model expresses actual facts.

The bend in the curve is convex to the KBr-H_2O axis of the diagram as previously predicted would be the case. In order, however, to test the assertion that the curvature of the eutectic valley is greater for salts having a greater difference in solubility, an experiment was carried out with silver chloride and potassium chloride. Silver chloride is comparatively only slightly less soluble than silver bromide and therefore should not affect the

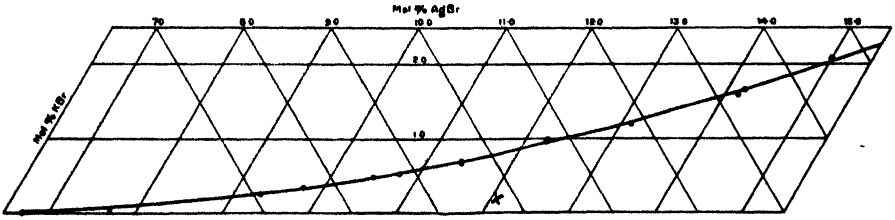


FIG. 5

shape of the eutectic valley greatly. Potassium chloride, however, is relatively much less soluble than potassium bromide and therefore this pair of salts should affect the shape of the valley greatly. Only one sample of the KCl-AgCl solution was taken and that at 90°C. Another point could be taken from Comey's tables. At 90°C the following mixture was found; 0.19 molar percentages silver chloride, 12.08 molar percentages potassium chloride and 87.73 molar percentages water. At 15°C the following results are recorded;[1] 0.013 molar percentages silver chloride, 7.53 molar percentages potassium chloride and 92.45 molar percentages water. These two results are shown in figure 5. The crosses are data on chlorides. The eutectic for AgCl-KCl[2] is at 70 molar percentages silver chloride and 309°C while for system, KCl-H_2O, it is at 5.6 molar percentages of potassium chloride and −11.1°C. The curve for the eutectic valley in the system, KCl-AgCl-H_2O projected on a plane, as in figure 1, must cross that of KBr-AgBr-H_2O in two places and since the curvature of the former is greater than that of the latter system, the differences

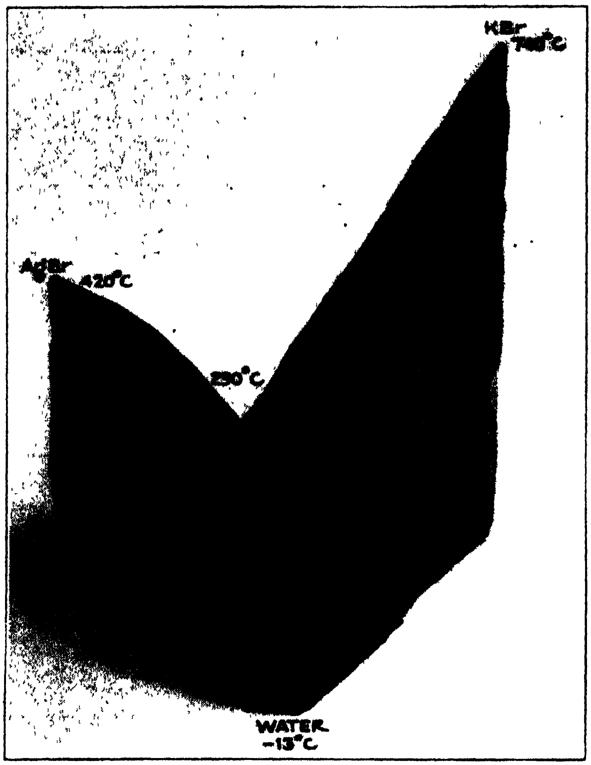


Fig. 6

---

[1] K. Schierholz: Akad. Wiss. Wien, 101 IIb, 8 (1890).

[2] S. F. Shemtshuskny: J. Russ. Phys. Chem. 7, 1052-53 (1906).

in relative solubilities is not the only factor of degree of curvature. If it were the only cause, then silver chloride should be more soluble in saturated potassium chloride than silver bromide in saturated potassium bromide at any temperature.

Some predictions can be made of solubility of silver bromide in saturated lithium bromide and sodium bromide. Lithium and sodium bromide[1] form mixed crystals with silver bromide in all proportions. In both cases, however, the alkali salts form water of crystallization, thus complicating the phase diagram at low temperatures. No very distinct eutectic can exist in the ternary system with both salts present in the solid phase and therefore no constant ratio of salts exist in solution at a given temperature as shown in the system, KBr-AgBr-H_2O in Fig. 4.

In order to ascertain more definitely that no compound existed between potassium and silver bromides from precipitates, powder x-ray diffraction photographs were made of the eutectic mixtures of fused silver and potassium bromides and of precipitates from saturated solutions of both salts from 100°C to 75°C, 75°C to 50°C and from 50°C to 25°C. These photographs show only the diffraction pattern of pure components, thus verifying the statement of Hellwig's previously referred to.

The author wishes to express his thanks to Mr. R. B. Wilsey for the x-ray examination of the various mixtures and to Dr. S. E. Sheppard for advice and criticism.

Rochester, N. Y.
April, 7 1926.

---

[1] A. Sandonnini and G. Scarpa: Atti Accad. Lincei, **22** II, 519-520 (1913).

THE POTENTIAL OF THE IRON ELECTRODE*

BY W. H. HAMPTON

The standard electrode potentials have been accurately determined for most of the common metals from electrodes possessing a high degree of constancy and reproducibility. However, one of the greatest difficulties met in potential measurements has been to obtain such an electrode from a form of iron that will represent the most stable state of this metal and which can be used in a reversible cell. There is described in this paper a series of electrodes and equilibrium measurements from which a value has been determined for the standard electrode potential of iron. This value can hardly be in error by more than a few millivolts and is much more accurate than anything published heretofore.

There has been only a small amount of work published dealing with a direct study of the electrode potential of iron, although much discussion occurs in the literature regarding the phenomena that are observed when this metal is involved in electrolytic processes. The most important work connected with the potential measurements is that of Richards and Behr,[1] who studied the e. m. f. of the cell, $Fe|FeSO_4(0.5M), KCl(0.1M), HgCl|Hg$. They used various kinds of iron and their results varied several hundredths of a volt, depending both upon the kind of iron and its previous treatment. By the use of finely divided reduced iron, constancy was obtained within about one centivolt, but because of the large liquid potential involved and because of the unknown activity of the Fe^{++} ion in such a concentrated solution, it is impossible to calculate from these measurements a value for the standard electrode potential.

Experimental Part

The cells used in the following experiments consisted of the elements $Fe|FeCl_2 (0.1M), HgCl|Hg$ and contained no liquid junction. Various concentrations of ferrous chloride were employed, but, for the most part, the measurements were made in one-tenth molal solutions and, unless otherwise stated, this will be the concentration referred to.

To prevent oxidation, an H-cell was used, which could be filled and kept free from air as much as possible. The two half-cells were provided with a glass stop-cock between them. The procedure in filling was to add about an inch of mercury to the calomel side and then evacuate this portion. Ferrous chloride solution saturated with calomel together with calomel paste was added by simply letting the vacuum draw in these materials. The other half of the cell was filled under an atmosphere of hydrogen and then stoppered to exclude the air. Complete connection was now made by opening the stopcock between the two cells.

---

* Contribution from the Chemical Laboratory of the University of California.

[1] Carnegie Inst. Pub., No. 61.

Standardized ferrous chloride solutions were prepared by dissolving powdered iron in hydrochloric acid following a similar procedure to that used by Richard and Behr in preparing their ferrous sulfate solutions. For the metal electrodes, three different varieties of iron were tried, an iron amalgam, finely divided iron and ordinary annealed iron.

Iron Amalgam: Measurements were made on amalgams which were prepared by electrolyzing a solution of ferrous sulfate, a method which was first discovered by Joule.[1] As iron is but very slightly soluble in mercury, it deposits as a suspended solid phase completely taken up and wetted by the mercury. Amalgam mixtures can thus be obtained varying in structure from liquid to almost completely solid in form, depending upon the amount of iron present. The iron in the solid phase is very finely divided as it gives no granular feeling whatever when rubbed between the fingers. The metal in these amalgams shows its ordinary reactivity, for on exposure to air a black film of oxide will immediately form on the surface of the mixture and, when water is present, rust will appear.

The sample for cell No. 1 was taken from an amalgam containing only a little solid phase in the liquid mercury. Cells No. 2 and No. 3 had for their electrodes amalgams of about the same consistency as soft putty, while the iron-mercury mixture for cell No. 4 was somewhat crumbly in structure.

Table I

Electrodes prepared from Iron Amalgams

	Cell No. 1		Cell No. 2		Cell No. 3		Cell No. 4
Time	Amalgam untouched.	Maximum after stirring.	Amalgam untouched.	Maximum after stirring	Amalgam untouched.	Maximum after stirring.	Amalgam untouched.
0	.7970		.8198		.8063		.8100
20 min.							.8147
2 hrs.							.8101
1 day	.7880		.8185		.8074		.8063
2 days	.7682	.8012	.8160		.7953		.8028
3 days	.7933	.8100	.8137		.7927		
4 days	.8001	.8106	.8101		.7907		
5 days	.7942	.8105	.8015	.8084	.7890	.8062	.7983
6 days				.8115			
13 days							.7970
20 days							*.7981
40 days							.7994

*New solution added.

---

[1] J. Chem. Soc., **16**, 378 (1863).

SAMPLE NO. 5—cell on which a series of measurements were made at different concentrations

Concentration	Potential			
.0095 Molal	.830 Max. Value			
.050 "	.8278 ± .0005	for period	15	days.
.0865 "	.8136 ± .0005	" "	30	"
.10 "	.8087 ± .0005	" "	5	"
.50 "	.7478 ± .0005	" "	13	"
2.245 "	.6668 ± .0005	" "	6	"
5.03 "	.5760 ± .0005	" "	8	"

It can be seen that the potential fell continually in all the cells on standing. Such an action results probably from the iron being used up on the surface and on bringing fresh material to the surface layer by stirring a higher potential is again obtained. As would be expected, the e.m.f. does not fall off so rapidly with the more solid amalgams. These cells as a whole, however, show the typical variations of potential measurements of iron which are hard to fully explain. Cell No. 2 and Cell No. 3, for example, were made up to be as nearly alike as possible.

The best explanation of differences encountered above seems to be that based on solubility phenomena. As the mercury completely covers the solid phase, the activity shown must be that of the metal in solution. The surface layer must always be a saturated solution to give the true activity of pure iron. We are confronted both with the possibility of a very slow rate of solution and with the exceedingly small solubility of iron in mercury. There is no means of telling directly whether or not any particular sample has for its surface film a saturated, unsaturated, or, perhaps, a super-saturated solution of iron. However, if all of the possibilities exist, some rough equilibrium should appear from which the potentials of an unsaturated solution would gradually decrease, and those of a super-saturated solution approach that equilibrium arising from the reaction of iron with water. The experiments support this idea somewhat. From these considerations, the best sort of amalgam would be one which had as large a percentage of iron as possible with just sufficient mercury to cover the surface. To obtain this condition, a portion of the material used in cell No. 4 was heated under a vacuum, and the mercury distilled off until the residue began to assume a dark gray color differing markedly from the bright lustre of mercury. This material (sample No. 5) gave one of the best cells for reaching a constant value, and a series of measurements were made in various concentrations of ferrous chloride. The value of .8087 volts for 0.1 molal solution checks that of .8136 volts for .0865 molal solution when the potentials are calculated for the same concentration.

The results for the amalgams in general indicate that the solid phase is not any compound formation of iron with mercury but is a finely divided suspension of the former metal, since the value .8087 volts checks very closely that of iron produced by reducing Fe_2O_3 with hydrogen.

Finely Divided Iron: Table II contains a series of measurements made on electrodes prepared from finely divided iron. The samples for cells numbers 6, 7 and 8 were prepared by reducing Fe_2O_3 with hydrogen which had been freed of all traces of oxygen and water vapor. For the material used in cell No. 6 the reduction was carried out at about 800°C for 24 hours. The reduced iron was withdrawn from the electric furnace, crumbled up, and hurridly packed around the platinum head at the bottom of the cell. There was considerable evidence of oxidation as the e.m.f. was quite low at first and then gradually increased. This was apparently due to a thin, oxidized film formed on the metal while being removed from the furnace and placed in the cell which was slowly dissolved, though not entirely, as the cell did not reach the accepted equilibrium value of the amalgam variety.

The sample used in cell No. 7 was made by reducing Fe_2O_3 under the same conditions as used for cell No. 6 except that an iron wire was placed in the Fe_2O_3 and on reduction this held the spongy mass of iron formed. Instead of powdering this up and placing it in the bottom of the cell, it was hung from the top immediately after withdrawing from the furnace. Cell No. 7 had the exceptionally constant value of .8088 volts which did not vary more than a tenth of a millivolt for thirty days. During this time, the solution was removed over the iron three times and each solution of ferrous chloride had been separately prepared.

The electrode of cell No. 8 was a sample reduced at 850°C which gave a high initial value. Richard and Behr attribute such high initial values to an active state of hydrogen occluded by the metal. However, the potentials

TABLE II

Electrodes prepared from finely divided iron

Time	Cell No. 6	Cell No. 7	Cell No. 8	Cell No. 9	Cell No. 10	Cell No. 11	Cell No. 12
0	.7778	.8017	.8316	.7884	.7962	.8390	.8108
10 min						.8462 max.	
15 "							.8202 max.
8 hrs.	.7942						
1 day	.8000	.8082	8216	.8048	.8018	.7997	.8102
2 days	.8026	.8084	.8152	.8058	.8024		
3 "	.8037	.8085	.8115	.8061	.8031		
4 "	.8042		.8099	.8065	.8035	.7908	.8052
5 "	.8043						
6 "			.8085	.8070	.8048		
8 "			.8086	.8077	.8048	.7906	.8032
10 "	.8047	.8087			.8052		
12 "	.8047	.8087	.8090	.8088			
15 "		.8088		.8090			
18 "		.8088					.8062
24 "		.8088					.8076
36 "		.8088					.8101

given by iron produced by reducing Fe_2O_3 which carbon monoxide (cells No. 11 and No. 12) had similar high values at the beginning. This iron contained considerable carbon after reduction and it is not known what effect this might have had. It seems improbable that carbon thus contained would increase the potential in any way. The writer is inclined to believe that these high initial potentials are due to exceedingly small particles of iron which are used up until the variation of activity with the size of particles has become negligible, and an equilibrium value around .8090 volts is established.

The electrodes of cells No. 9 and No. 10 were a variety of Kahlbaum's C. P. iron powder which had been reduced a second time before placing in the cell. These agreed fairly well with the constant cell. Both the electrodes were of the same material and given as nearly as possible the same treatment. This again illustrates the type of differences in measurements which are constantly met and hard to account for.

Annealed Iron: Turning now to the series of measurements made with annealed iron as electrodes, it will be unnecessary to explain any of the experiments in detail as all the plain wire electrodes behaved similarly, giving considerably lower values than the finely divided form. No equilibrium value can be assigned to this form of iron, but, in general, the potential was about .05 volts lower than the other varieties. At times, samples approach the value of the finely divided form within .03 volts. Making the iron the cathode by simply leaving the working battery of the potentiometer slightly unbalanced against it, the e. m. f. would rise at a much faster rate than could be accounted for by polarization resulting from concentration changes, for, by placing the same electromotive force (one or two tenths of a milivolt) on several types of cells not in connection with this work, there was no effect whatever. In like manner, by making the electrode serve as an anode, the potential would decrease. This seemed to confirm the idea that iron in the annealed form has always a more or less passive state when immersed in water solutions and that the true activity may be very near that of the reduced iron. Furthermore, the same sample gave values more nearly that of finely divided iron in solutions of higher concentrations, differing .03 volts and, at times, approaching the higher value within about 01. volts.

For a final test of this idea, which seems quite conclusive, it was proposed to use some ionizing agent other than water with which the iron would not react. The only available medium was an eutectic mixture of lithium and potassium chloride. Ferrous chloride previously dehydrated and dried under an atmosphere of hydrogen chloride was added to the eutectic mixture. The resulting mixture of fused salts was further dried by first passing dry hydrogen chloride through the mixture and then hydrogen. Annealed iron wire served as one of the electrodes and finely divided reduced iron as the other. Two cells were thus made up using separately prepared electrodes. One of these showed finely divided iron to be more active by 2.3 ± .3 millivolts. The temperature of this cell was maintained at 380°C by a fused nitrate bath. The other showed a slightly greater difference, remaining constant at 3.3 ± .3 millivolts and the temperature was varied from 350°C to 450°C. We would naturally expect to get small differences of this order of magnitude, which are attributed to the relative state of subdivision. The true activity of annealed iron is therefore very near that of finely divided iron, and the large difference shown in aqueous solutions must be due to passivity of the annealed form incurred by water.

Table III contains a series of measurements using iron wires for the electrodes. The electrode of cell No. 13 was a plain iron wire that had been heated for 36 hours at 850°C in the reduction furnace and allowed to cool slowly.

The wire in cell No. 14 was superficially oxidized by heating and cooling in air for several times and then reduced in the furnace.

The wire in cell No. 15 had been set in water until a large amount of rusting had taken place. It was then reduced by hydrogen.

The electrode of cell No. 16 was dipped in dilute hydrochloric acid for several minutes. It was then washed in 0.1 M ferrous chloride and placed in the cell.

The wire in cell No. 17 was simply sand-papered before placing in the cell.

TABLE III

Electrodes prepared from iron wire

Time	Cell No. 13	Cell No. 14	Cell No. 15	Cell No. 16	Cell No. 17
0 days	.7190	.7703	.8052	.7486	.7490
2 "	.7409	.7798	.7797	.7800	.7912
4 "	.7484	.7834	.7773	.7793	.7575
6 "	.7506	.7835	.7773	.7807	.7580
8 "		.7830	.7774	.7532	.7592
10 "					.7696
12 "					.7800
16 "	.7515				.7803
24 "	.7578				.7719

	Cell No. 18	Cell No. 19	Cell No. 20
0 "	.7140	.6864	.7475
2 "	.7095	.7189	.7592
4 "	.7106	.7160	.7492
6 "	.7153		.7484
8 "	.7270		.7484
10 "	.7330	.7377	
12 "	.7302	.7259	
16 "	.7350	.7186	

The electrodes of cells No. 18 and No. 19 received the same previous treatment as those of No. 16 and No. 17 respectively, but the measurements were made in .500 M ferrous chloride solution.

Cell No. 20 is shown for comparison having for its electrode reduced iron oxide in .500 M ferrous chloride solution.

Measurements at various concentrations: Only a few cells were measured in concentrations other than one tenth molal. In all cases, the nature of the variations was the same. In the more concentrated solutions the variations as a whole were not quite so great. However, for solutions as dilute as .01 M no samples would give a constant value within any reasonable time. The tendency in dilute solutions was to decrease continually for a long period of time.

Calculation of Results

Choice of results for calculation: The measurements given comprise only a small amount of the total number made, but they are selected to show the typical variations as well as to present all the peculiarities involved in this study of iron. In many ways, they duplicate the observation of others, but additional experiments were carried out to test new ideas which made it possible to arrive at a more truly representative value of the activity of iron. The most constant value given by any sample was that of cell No. 7, namely .8088 volts in .1 M ferrous chloride solution. Several cells remained constant for long periods of time within a few tenths of a millivolt of this potential. Furthermore it was approached from both directions. For constant values at other concentrations, we have the series of measurements with sample No. 5. There is no check on the results in concentration above .1 M for there are no data at hand to make the necessary calculations. However, the values for .0865 M, .05 M and .0095 M can be used and are tabulated in Table IV.

Calculation of Results: When two faradays of electricity pass through the cell $Fe\,|\,FeCl_2(aq),\ HgCl\,|\,Hg$, the following reaction takes place

$$Fe + 2\ HgCl = Fe^{++} + 2Cl^{-} + 2\ Hg. \qquad (1)$$

The electromotive force is given by the equation

$$\begin{aligned} E &= E^\circ - RT/2F \ln 4\gamma^3 m^3 \\ &= E^\circ - 0.08873 \log \sqrt[3]{4}\,\gamma m \qquad (2) \end{aligned}$$

in which E° is the potential when the activity of the ferrous chloride is unity, m is the molal concentration and γ the activity coefficient.[1]

As there are no data at hand from which the activity coefficients of ferrous chloride can be calculated, the values for barium chloride were taken at corresponding concentrations. The justification for doing this arises from the fact that the chlorides of the bivalent salts as a class with the exception of $HgCl_2$ and $CdCl_2$ behave very similarly. For example, the solubilities of thallous chloride in .1 to .01 molal concentrations of ferrous chloride were found to be the same as that given by Bray and Winninghof[2] for barium chloride. In column 2 of Table IV are given the activity coefficients obtained by plotting the values which have been accurately calculated by Lewis and Randall for barium chloride from freezing point data against concentration and interpolating for various concentrations.

---

[1] Lewis and Randall: "Thermodynamics," Chapter XXIX (1923).

[2] J. Am. Chem. Soc., 33, 1663 (1911).

TABLE IV

m	γ	E	E°
.100	.501	.8088	.7113
.0865	.516	.8136	.7117
.050	.563	.8278	.7095
.0095	.719	.8830	.7090

From a review of the discussion of the different measurements, the most probable value for E° is that calculated for .1 M and we may then write the equation:

$$\mathrm{Fe}|\mathrm{FeCl_2}\ (\mathrm{aq.}),\ \mathrm{HgCl}|\mathrm{Hg} : E° = .7113 \qquad (3)$$

The Normal Electrode Potential: To calculate the normal electrode potential, we make use of the cell[1]

$$\mathrm{H_2}|\mathrm{HCl}\ (0.01\mathrm{M}),\ \mathrm{HgCl}|\mathrm{Hg}: E = .5105 \qquad (4)$$

and using for the activity coefficient[2] of 0.01 M HCl, $\gamma = .924$ we obtain:

$$\mathrm{H_2}|\mathrm{HCl},\ \mathrm{HgCl}|\mathrm{Hg} : E° = .2700 \qquad (5)$$

Since all the factors of equations (3) and (5) are of activity one we may write them in the form

$$\mathrm{Fe}|\mathrm{Fe^{++}}\ \|\ \mathrm{Cl^-},\ \mathrm{HgCl}|\mathrm{Hg} \qquad E° = .7113$$
$$\mathrm{H_2}|\mathrm{H^+}\ \|\ \mathrm{Cl^-},\ \mathrm{HgCl}|\mathrm{Hg} \qquad E° = .2700$$

Combining these two equations gives

$$\mathrm{Fe}|\mathrm{Fe^{++}},\ \mathrm{H^+}|\mathrm{H_2} \qquad E° = .4413 \qquad (6)$$

Since $(\mathrm{H_2}|\mathrm{H^+})$ is taken as zero, we arrive at the value E° = .4413 for the normal electrode potential of iron. The reliability of this value will be discussed further after considering the results obtained by equilibrium measure ments which are to follow.

Equilibrium Measurements

Since the potential of the thallium electrode is near that of iron, it seemed possible to find some equilibrium that involved mutual oxidation and reduction of these metals. With data already at hand the equilibrium

$$\mathrm{Fe} + 2\ \mathrm{TlCl} = \mathrm{Fe^{++}} + 2\ \mathrm{Cl^-} + 2\ \mathrm{Tl}$$

would permit an easy calculation of the iron electrode potential provided the concentration and activity of the ferrous chloride could be determined. Preliminary experiments showed that the reaction would proceed in either direction although the rate was quite slow.

From these observations, a one-liter flask was fitted with four 100 cc containers connected to the neck so that samples could be withdrawn for analysis. To the flask were added 40 grams of thallous chloride, 8 grams of powdered reduced iron, and 700 cc of water. The filling was carried out under an atmosphere of hydrogen to prevent any oxidation. The vessel was then evacuated and sealed from the air. This mixture was placed in a thermostat at 25°C and continually agitated by a mechanical shaker.

---

[1] Lewis, Brighton and Sebastian: J. Am. Chem. Soc., **39**, 2245 (1917).

[2] Lewis and Randall: "Thermodynamics," Chapter XXVI (1923).

The sample tubes were removed from time to time and portions of the solution were rapidly weighed out and added to dilute hydrochloric acid. A titration was then made with .05 N potassium permanganate, a method used by A. A. Noyes[1] for the quantitative determination of thallium. The end point was somewhat masked by the yellow color of ferric iron but by having a comparison solution present it could be judged within two drops of .05 N potassium permanganate. Check experiments showed this method to be accurate within 0.5 per cent. This gave the total number of equivalents to oxidize both the iron and the thallium. The total chloride ion content was determined in a second portion of the solution acidified with nitric instead of hydrochloric acid. From a result of these two determinations we can calculate the separate concentrations of ferrous chloride and dissolved thallous chloride from the relations:

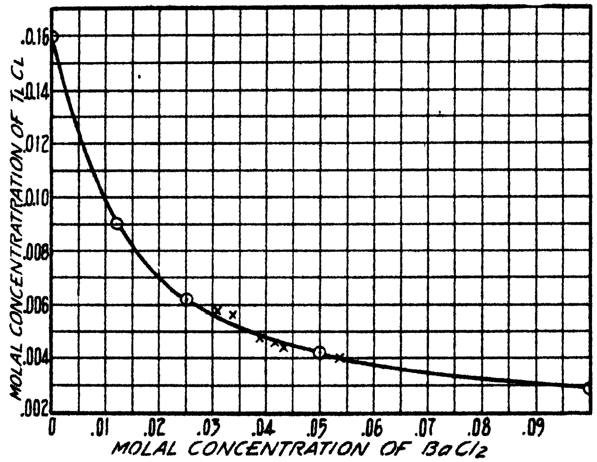


FIG. 1

$$2\ Fe^{++} + Tl^{+} = \text{total concentration of } Cl^{-}$$

$$Fe^{++} + 2Tl^{+} = \text{total no. of equi. } K\ MnO_4$$

It was found that the solubility of thallous chloride in solutions of ferrous chloride is practically the same as in solutions of barium chloride of like concentrations. The curve in Fig. 1 represents the solubility of thallous chloride in varying concentrations of barium chloride[2] and the crosses that in ferrous chloride. By the use of this curve and the titration with potassium permanganate the composition of sample portions could be determined with sufficient accuracy for calculations which are to follow later.

Table V gives a series of analyses made upon the mixture described above, and it shows how slowly the reaction proceeds toward equilibrium. Most of the reaction took place within the first nine days, at the end of which time the concentration of ferrous chloride became .0306 M and only increased to .0453 M after a period of three months. When all the sample flasks had been removed from the larger vessel, the remaining contents were removed with as little exposure to air as possible and placed in a smaller container. The last two analyses were made on portions taken from this vessel when the amount of solution became exhausted. While these analyses indicate equilibrium, it is doubtful whether this point was yet reached for the shaking had been intermittent during the last period. The rate of reaction of this type depends very largely upon the agitation.

---

[1] Z. physik. Chem., 9, 603 (1892).

[2] Bray and Winninghof: J. Am. Chem. Soc., 33, 1663 (1911).

There was no exception to the behavior of iron in these experiments of showing apparently different activities as in the electrode measurements. Several mixtures in smaller amounts were made up and these behaved differently. After equal intervals of time, in some mixtures there appeared to be no reaction at all, while varying amounts of thallium were formed in others. None of these however appeared to be more reactive than the one for which the analysis is given in Table V.

There was even more difficulty in approaching the equilibrium by the reduction of ferrous chloride with metalic thallium, and, while the reaction is known to proceed, the rate is very slow. The speed of such a reaction necessarily depends to a large extent upon the amount of metalic surface exposed

TABLE V

Mixture made up with 40 grams TlCl, 8 grams iron and 700 cc water

Time of analyses	Equi. of $KMnO_4$ per 1000 gm. sol.	Molal conc. $Fe\,Cl_2$	Molal conc. Tl Cl
0 days	—	—	01607
9 "	.0423	.0308	0057
21 "	.0437	.0333	0053
31 "	.0478	.0388	.0047
60 "	.0507	.0416	0046
83 "	.0524	.0435	.0043
90 "	.0531	—	—
102 "	.0533	.0453	.0042

TABLE VI

Equilibrium Measurements, $FeCl_2 + 2Tl$

Sample Number 1.		Sample Number 2.	
Time	Equi. of $KMnO_4$ in 1000 grams sol.	Time	Equi. of $KMnO_4$ in 1000 grams sol.
0 days	.0950	0 days	.1010
8 "	.0865	6 "	.0999
15 "	.0768	14 "	.0968
22 "	.0710	21 "	.0942
		28 "	.0920

and, for a soft metal like thallium, it is hard to produce a finely divided condition. Experiments were tried with small shavings of metallic thallium and a solid material from a saturated thallium amalgam. These gave only more or less qualitative results and nothing definite enough to be used in calculations. Later a method of approaching equilibrium from this direction was tried but time did not permit carrying this work to completion. Mixtures were prepared by reducing thallous chloride with excess iron powder and undissolved salt. The thallium separates out as small particles and remains for the most part in this condition. Table VI gives the results of two experiments on such mixtures beginning with one tenth molal ferrous chloride. Sample No. 1 was the residue from the run given in Table V and No. 2 was that of a separately prepared mixture. The latter was in a flask and did not permit mechanical agitation and was only shaken from time to time by hand.

It is evident that neither sample had reached equilibrium when the last analyses were made. At this time the solution over the mixture in No. 1 became exhausted and the work was discontinued.

Calculation of Results

Equation (7) can be expressed in the following cell reaction:

$$\mathrm{Fe}\,|\,\mathrm{FeCl_2}\ (\mathrm{aq}),\ \mathrm{TlCl}\,|\,\mathrm{Tl}$$

the e. m. f. of which is given by equation (2)

$$E = E^\circ - .08873 \log.\ 1.588\gamma m$$

Assuming equilibrium when the last analysis was made of the mixture given in Table V, we then have

$$E^\circ = .08873 \log.\ 1.588\ \gamma\ .0453 \qquad (8)$$

To determine γ we take the activity coefficient of barium chloride of the same ionic strength as the solution of ferrous chloride and thallous chloride which corresponds to a molality of .0467. The activity coefficient for this concentration is .574. Substituting this value for equation (8) and solving for E° we obtain

$$\mathrm{Fe}\,|\,\mathrm{FeCl_2}\ (\mathrm{aq}),\ \mathrm{TlCl}\,|\,\mathrm{Tl} : E^\circ = -.1228 \qquad (9)$$

Combining this with the equation[1]

$$\mathrm{Tl}\,|\,\mathrm{TlCl},\ \mathrm{HgCl}\,|\,\mathrm{Hg} : E = .8246$$

we obtain

$$\mathrm{Fe}\,|\,\mathrm{FeCl_2}\ (\mathrm{aq})\ \mathrm{HgCl}\,|\,\mathrm{Hg} : E^\circ = .7022$$

Considering the equilibrium now as approached from right to left and making similar calculations for the last analysis of samle No. 1 given in Table VI, we have

$$\mathrm{Fe}\,|\,\mathrm{FeCl_2}(\mathrm{aq}),\ \mathrm{HgCl}\,|\,\mathrm{Hg} : E^\circ = .7135$$

---

[1] Gerke: J. Am. Chem. Soc., **44**, 1684 (1922).

Discussion of Results

It has been shown that the reaction expressed by equation No. 7 has been made to approach equilibrium in both directions. Assuming equilibrium at the times of the last analyses, the E° values for equation (3) differ by .0113 volts, but it is certain that in neither case had the reaction ceased. Furthermore, all the observed values of Table IV lie between these two. The following values have been given for comparison:

(a) From the equilibrium measurement: $2TlCl + Fe: E^\circ = .7022$
(b) From electromotive force: $E^\circ = .7113$
(c) From the equilibrium measurement: $FeCl_2 + 2Tl: E^\circ = .7135$

By examination of Table V and VI we would more likely expect the value of (c) to be too high and that of (a) to be too low. Although predictions of this kind may seem a little questionable when so many factors have to be considered as those involved in this equilibrium, nevertheless electromotive force measurements on iron in a finely divided condition, whether the amalgam variety or the reduced oxide, show quite conclusively that the value of E° can be but very little if any lower than that given for (b).

In round numbers, then, the normal electrode potential is taken as .4410 volts for all ordinary forms of iron, a value which is in all probability correct within three millivolts.

Summary

The potential of several varieties of iron was measured in the cell $Fe \mid FeCl_2$ (aq), $HgCl \mid Hg$ in which there was no liquid junction.

An amalgam variety prepared by electrolyzing a solution of ferrous sulfate, using a mercury cathode, gave .8090 volts as the best equilibrium value in 0.1M ferrous chloride.

Finely divided iron prepared by reducing Fe_2O_3 gave .8088 volts as the best equilibrium value in 0.1 M ferrous chloride.

Potentials of annealed iron in water solutions were much lower than those obtained with the other varieties. By measuring the potential between finely divided iron and the annealed form in a solution free from water and consisting of ferrous chloride in a fused eutectic mixture of lithium and potassium chloride it was found that there was very little difference between the activity of each. The difference in water solutions was attributed to passivity of compact iron in contact with water.

The value .4413 volts was calculated from the above measurements as the most probable value of the normal electrode potential, and it is not considered in error by more than three millivolts. Measurements made on the equilibrium $Fe + 2\ TlCl = Fe^{++} + 2\ Cl^- + 2\ Tl$ substantiated this conclusion.

A NOTE ON THE MECHANISM OF EMULSIFICATION*

BY ALFRED J. STAMM AND ELMER O. KRAEMER**

The suggestion that the phase relations (*direction* of curvature of interface) and size of particles (*magnitude* of curvature of interface) in emulsions are determined by the orientation of *wedge-shaped* molecules of stabilizer in the interface between disperse phase and dispersion medium[1] has greatly stimulated interest in the problem of emulsions and emulsification. However, the rosy promises at first held out by this oriented wedge theory of emulsions unfortunately have not materialized. Two claims have been made for the theory: first, that it explains the decrease in the most probable size of particles with a change in emulsifying agent from sodium to potassium to cesium soaps; second, that it explains the change in phase relations upon changing emulsifying agent from an alkali soap to an alkaline earth, or an iron or aluminum soap. Neither the original evidence for the theory nor the consequences predicted by the theory have been completely confirmed. The *number*-distribution curves[2] (showing the distribution of total number of particles among the various sizes present) does not provide an appropriate basis for correlating the sizes of the particles in an emulsion with the supposed wedgeness of the stabilizing molecules. Rather, a test of the wedge theory requires a comparison of *surface*-distribution curves of emulsions with different stabilizing agents.[3] A logical application of the wedge theory would lead one to expect a decrease in the *radius of curvature* most frequently occurring in the interface with an increase in the wedgeness of the emulsifying agent molecules; and it is the maximum of the *surface*-distribution curve which defines the most probable radius of curvature of interface in the emulsion. But for practical purposes of expressing the degree of dispersion of dispersed systems, the *mass*-distribution curve[4] is usually to be preferred.[5]

Since the maximum of the surface-distribution curve corresponds to a greater radius of particle than does the maximum of the related *number*-distribution curve, the most probable radius of curvature in an emulsion stabilized by sodium oleate, as quoted by Harkins,[6] is even more than 750 times the apparent length of the oleate molecules. It therefore seems rather unlikely that the oleate molecules, by virtue of *their presumed wedge-shape,* determine to any essential degree the radius of curvature of such relatively large drops.

---

* Contribution from the Laboratory of Colloid Chemistry, University of Wisconsin.

** Fellow of the National Research Council.

[1] Langmuir: J. Am. Chem. Soc. 39, 1848 (1917): Harkins: 39, 354, 541 (1917); Bogue's "Colloidal Behavior," Chapter VI (1924); Finkle, Draper and Hildebrand: J. Am. Chem. Soc., 45, 2780 (1923); Harkins and Keith: Science, 59, 463 (1924); Harkins: Paper given before Second Colloid Symposium (1924) and partially published in monograph.

[2] Finkle, Draper, and Hildebrand: loc. cit.; Keith: Thesis, Univ. Chicago, (1924); Harkins and Keith: loc. cit.

[3] Stamm: Third Colloid Symposium Monograph (1925).

[4] See earlier papers of authors.

[5] In their most recent paper, Harkins and Beeman (Proc. Nat. Acad. Sci., 11, 631 (1925)) present all three types of distribution curves; i. e., number, surface and volume (same as mass.)

[6] In Bogue's "Colloidal Behavior," p. 201.

In the second place, mass and surface-distribution curves determined by sedimentation and microscopic[1] methods have failed to reveal any significant variation in the position of the maxima for emulsions with palmitates of sodium, potassium, or cesium as stabilizers, although originally reported by Finkle, Draper, and Hildebrand, and by Harkins and Keith. This inconsistency may be due either to differences in the methods of emulsification, i.e., differences in mechanical treatment—or to inadequate microscopic measurements by the authors last named.[2] Furthermore, the total interface in the emulsions has been found to be constant, within the limits of experimental errors, for the palmitates of sodium, potassium, and cesium.[3] Other difficulties in the oriented wedge theory of emulsification have arisen. Thus, although the influence of alkali soap (univalent cation), in the presence of an excess of the corresponding alkali, upon the degree of dispersion of emulsions[4] may apparently be harmonized with the wedge theory by supposing the excess of alkali to repress hydrolysis, the same line of reasoning in the case of excess of barium hydroxide with a barium soap leads to expectations which are flatly contradicted by the facts. It seems hazardous also to suggest—as has been done—that aluminum or iron soaps function as emulsifying agents in the form of single molecules nicely oriented in the interface, in view of the instability of these soaps, and the observation by Briggs and Schmidt[5] that flocks of what is perhaps aluminum hydroxide exist in emulsions stabilized by the use of an aluminum soap. A similar difficulty appears in the inconsistency between facts and the wedge theory predictions concerning the relative influence of potassium palmitate and potassium chaulmoograte upon the degree of dispersion of emulsions.[6] Again, phenol gives rise to oil-in-water emulsions, contrary to what one might expect if the wedge theory is so applied as to assume the C_6H_5 nucleus to orient into the "oil" and the OH to enter the water phase. Likewise, on the basis of the wedge theory, there is no apparent reason for expecting or means of explaining *reversals in phase relations* in a series of aqueous emulsions of various petroleum distillate fractions (varying viscosity), stabilized by casein.[7] The usefulness of the wedge theory in other phase-relationship problems presented in this paper is also not obvious. It has not yet been shown how the oriented wedge theory of emulsions can be reconciled with *reversal of phase relations* brought about by a change in the volume composition of an emulsion, even in the presence of sodium oleate,[1] or in the character of the walls of the container.[2] Even the assumption of 100% dissociation of the oriented soap molecules does not relieve the oriented wedge theory of the responsibility of predicting unequal radii of curvature with different emulsifying agents, for if such thin films (monomolecular) were directly effective in determining radius of curvature, variation in cation might be expected to so modify the "foundation" of the film[3] as to change the film properties and the normal radius of curvature.

---

[1] Kraemer and Stamm: J. Am. Chem. Soc., **46**, 2709 (1924); Stamm and Svedberg: **47**, 1582 (1925); Stamm: Third Colloid Symposium Monograph (1925).

[2] In a recent paper, Harkins and Beeman (Proc. Nat. Acad. Sci., **11**, 631 (1925)) admit the independency of the positions of maxima in surface and mass distribution curves with respect to the soap used as emulsifier (Na, K, and Cs).

[3] Stamm: Third Colloid Symposium Monograph (1925).

[4] Harkins: loc. cit.; Stamm and Svedberg: loc. cit.

[5] Briggs and Schmidt: J. Phys. Chem., **19**, 491 (1915).

[6] Harkins and Beeman: loc. cit.

[7] Seifriz: J. Phys. Chem., **29**, 587 (1925).

It seems therefore that considerable experimental evidence is positively contrary to the consequences of the oriented wedge theory, as stated thus far, while direct evidence in favor of the theory is largely lacking. On the other hand, numerous observations of the influence of volume composition and methods of emulsification and homogenization upon phase relations and the degree of dispersion of an emulsion have led the authors to the suspicion that the *shapes* and *sizes* of the molecules of stabilizing agents perhaps have been over-emphasized in this connection.

It should be remembered that the phase relations and the degrees of dispersion of an emulsion prepared by dispersion are the net results of two opposing processes, namely, a pulverizing process and a coagulating process.

The first, or pulverizing process, is accomplished by shaking, mixing, the use of colloid mills, homogenizers, etc., and probably consists in the mutual pulverization of the two liquid phases by the formation and subsequent disruption into drops of lamellae and threads of one liquid in the other, either by flowing processes or by impact of liquid masses against each other or the walls of the container. In this stage, the dissipation of mechanical energy in the system gives rise to hydrodynamic problems of great complexity. Although it would be very difficult to correlate them quantitatively, the factors of importance may be said to be mechanical and hydrodynamic ones, and include the particular mechanical treatment, character of solid walls, volume composition, densities, viscosities, interfacial tensions and surface tensions (if a gas is present, as in shaking a partially filled bottle) of the liquids.

The relative extents to which the two liquids are drawn out into lamellae and threads in each other are probably determined principally by the volume composition, viscosities and densities of the liquids. (The interfacial tension, being the same for either phase, has a symmetrical influence upon the formation of lamellae of both liquids.[4]) This process of lamellae formation is of primary importance in determining the degree of dispersion of an emulsion. A liquid thread or lamella is unstable, however, and spontaneously breaks up into drops. Thus, a liquid cylinder is unstable when its length is greater than three times its diameter.[5] The manner in which the disruption of the lamellae into drops takes place may be considered as largely dependent upon the magnitude of the lamellae and the interfacial tension and the viscosity of the lamella phase. When the interfacial tension is very high and the viscosity low, as in the case of water-mercury,[1] the dispersion of lamellae into unusually small drops is very striking. Although the interfacial tension is a factor in the disruption of lamellae, the thickness of the lamellae and the sizes of the drops make it improbable that the *shapes and sizes of the molecules* in the interface have any direct mechanical or "geometrical" bearing upon the sizes of the drops formed.

---

[1] Sanyal and Joshi: J. Phys. Chem., **26**, 481 (1922). This type of reversal was *confirmed* in this paper.

[2] Wa. Ostwald: Kolloid-Z., **6**, 103 (1910). Also confirmed in this paper.

[3] Goard and Rideal: J. Chem. Soc., **127**, 1668 (1925).

[4] Compare with Donnan: Z. physik. Chem., **46**, 197 (1903).

[5] Winkelmann: Handbuch Physik, I²

These same factors, i. e. mechanical treatment, volume composition, viscosity, density and interfacial tension, are probably involved in the dispersion of a liquid mass by impact. Impact gives rise to lamellae which break into drops. The work of disruption by impact, like the work of deformation of small drop[2] may increase with the interfacial tension and with a decrease in a the size of the liquid mass to be broken. In this process, a decrease in interfacial tension probably facilitates dispersion—but, certainly, it is difficult to recognize how the *shapes and sizes* of molecules in the interface could directly and mechanically determine the sizes of the drops formed on such a gross scale. In the realm of magnitudes here involved, the interfacial tension is practically independent of the radius of curvature of the interface. Both phases are dispersed in the process of mixing, shaking, etc.

Simultaneously and subsequently to the pulverization process is the second major process—the coagulation or reunion of the drops of the dispersed liquids to form continuous phases. The rates of coagulation may be taken to depend primarily upon the viscosities, densities, volumes, and interfacial tensions in a fashion which cannot be accurately specified: The rates may, and usually do, differ for the two liquids, especially if an "emulsifying agent" be present. One liquid, because of a lesser degree of pulverization, a greater rate of coagulation, or both, may unite to form a continuous phase—the dispersion medium—in which the second liquid forms the disperse phase because of greater degree of pulverization in the first stage, or a smaller rate of coagulation in the second stage, or both. The phase relations and the degree of dispersion, or distribution of size of particle of an emulsion thus are presumed to be determined by these two opposing processes.

In the case of two pure liquids, the rates of coagulation of both may be great, and the emulsion is said to be unstable, for it more or less quickly "breaks" into two separate phases. Upon the addition of an "emulsifying agent," in moderate concentration (as a few hundredths molar soap solution) the pulverization process may not be greatly modified.[3] Only the interfacial tension is significantly changed, which means that the rates of coagulation may be most profoundly modified. Presumably, the rate of coagulation of the drops of one liquid is very much decreased, while the drops of the other liquid reunite to form a dispersion medium for the drops which are protected from coagulation by a stabilizing film of unknown nature. By virtue of the protection afforded the drops, they may "cream" without breaking, and the emulsion is said to be stable. The protecting film, to be effective, must form fairly quickly, before coagulation of the unprotected drops has progressed too far. Since the rapid formation of a film partially depends upon the tendency of the interfacial tension to be decreased by the added agent, it is clear why substances which have markedly lower interfacial tensions (as the soaps) are frequently effective emulsifying agents—or rather stabilizing agents. Thus, the stabilizing agent may influence the primary process of dispersion only indirectly by modifying what may be called mechanical or hydrodynamic factors operating during the pulverization process. The maximum degree of dispersion is fixed before the stabilizing agent steps in to protect the drops of one phase from reuniting. The greatest influence of the emulsifying agent is probably upon the coagulating process; it thus may overshadow other factors and determine the phase relationship of the final emulsion. The coagulating process in an emulsion, as that of an oil-in-water emulsion stabilized with sodium soap to which has been added $CaCl_2$, is probably very similar to coagulating processes in other suspensoids. In neither case does there seem to be any possibility of recognizing the influence of the *geometrical shapes and sizes* of the stabilizing molecules.

---

[1] Nordlund: Kolloid-Z., **26**, 121 (1920).

[2] Hatschek: Kolloid-Z., **7**, 81 (1910).

[3] Yet, *any* modification makes it impossible to preserve *uniform* and *comparable* conditions of mechanical treatment during the pulverization process—when different emulsifying agents are used.

Further examples of the manner in which these factors superimpose are given in diagrammatic form in Tables I and II. Pairs of incompletely miscible liquids (1 : 1 by volume) were shaken and the phase relations of the resulting emulsions[1] observed. The denser liquid is placed below the lighter in the diagram, and the arrow indicates the direction and qualitative extent to which one liquid became dispersed in the other. One series of liquid pairs with water as a common member, and one series with glycerine as a common member are given with data on viscosities, surface tensions,[2] and interfacial tensions when available. In addition, there are given observations upon the influence of magnesium palmitate, potassium palmitate, or of oleic acid upon the phase relationship for these same liquid pairs.

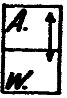
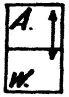
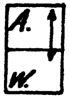
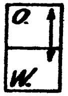
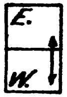
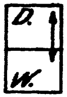
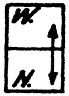
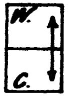
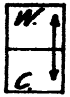
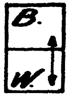
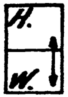
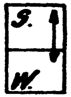
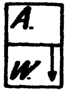
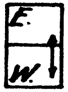
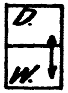
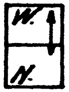
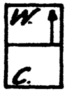
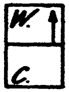
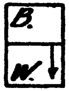
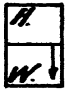
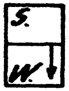
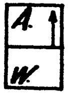
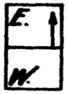
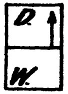
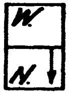
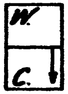
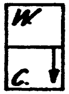
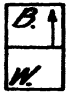
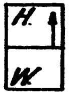
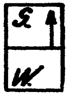
In the case of the pairs in the water series, it may be noted that in each and every case examined, the less viscous liquid tended to remain dispersed in the more viscous phase, suggesting therefore either that during the pulverizing process, lamellae of the more viscous liquid were formed to a much less ex-

---

[1] The question may be raised as to whether such systems, usually unstable, may be properly called emulsions. It seems evident, upon consideration, that the differences between these systems and those made more stable by the addition of a stabilizing agent are differences not in kind, but only in degree. In any case, it must be admitted that the stabilized systems are more complicated, and that the factors of mechanical treatment, volume composition, viscosity, interfacial tension, etc., which play a part in determining the phase relations and size of particles in the simpler systems *without* monomolecular layers of stabilizing molecules must also be important in determining phase relations and size of particles in the systems *with* added stabilizing agents.

[2] Most of the surface tension data were taken from Harkins, Clark, and Roberts: J. Am. Chem. Soc., 42 700 (1920).

Table I
Water Systems.

	Isoamyl alcohol	Isobutyl alcohol	n-Butyl alcohol	Oleic acid	Ethyl acetate	Dimethyl aniline	Nitro-benzene	Chloroform	Carbon tetra-chloride	Benzene	Heptane	Stanolax
Phase relationship	 A. W.	 A. W.	 A. W.	 O. W.	 E. W.	 D. W.	 W. N.	 W. C.	 W. C.	 B. W.	 H. W.	 S. W.
Visible	1 min.	1 min.	5 sec.	.5 min.	5 sec.	10 sec.	<5 sec.	<5 sec.	<5 sec.	<5 sec.	<5 sec.	10 sec.
Complete separation	15 min.	15 min.	2 min	15 min.	1 min.	1 min.	1 min.	10 sec.	10 sec.	10 sec.	15 sec.	5 min.
Relative viscosity	4.58	4.03	—	very viscous	0.45	1.28	1.80	0.55	0.96	0.62	.040	very viscous
Surface tension	24.1	22.8	24.5	32.5	26.5	38.3	43.5	26.5	26.9	28.8	19.0	—
Interfacial tension	4.4	1.8	0.4	15.7	18.0	25.8	25.7	32.6	43.3	36.0	50.4	—
Effect of adding oleic acid		 A. W.		—	 E. W.	 D. W.	 W. N.	 W. C.	 W. C.	 B. W.	 H. W.	 S. W.
Effect of adding magnesium palmitate		 A. W.		—	 E. W.	 D. W.	 W. N.	 W. C.	 W. C.	 B. W.	 H. W.	 S. W.

tent, or that the rate of coagulation of the more viscous liquid was the greater. The complexity of relationships to be met are, however, shown when reference is also made to glycerine systems; for here the very viscous glycerine became the dispersed phase in every case. These two cases of maximum simplicity (i. e., two single liquids) illustrate the complexity of the emulsification process as a hydrodynamic proposition.

Influences of volume composition upon phase relationship may be seen also in the case of two liquids. Oleic acid-water mixtures with a volume per cent of oleic acid between 5-70% were passed through the colloid mill four times. For volume compositions of 5-40% oleic acid, the oleic acid was the dispersed phase. But with compositions of 45-70% oleic acid, the water was the dispersed phase.[1] It seems safe to assume that these differences indicate the influence of volume composition upon the process of lamellae formation and their disruption into drops.

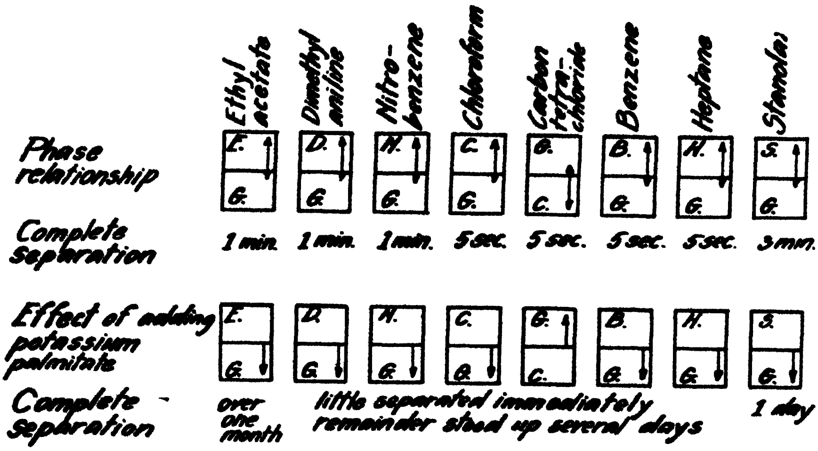


Table II
Glycerine Systems

It is of interest to observe the influence of benzene upon the emulsions in the region of phase reversal. To a water-in-oleic acid emulsion (45% oleic acid) 10 cc. of benzene were added and the mixture passed through the colloid mill, but without reversal. A further addition of 10 cc. of benzene and repassage through the mill gave an oleic acid-benzene-in-water emulsion just over the reversal boundary region.

Volume composition effects can also be observed with mixtures of stanolax and water, although coagulation is more rapid than in the preceding case. With 50% oil, water was the dispersed phase, but with 40% oil, the oil was the disperse phase. The latter mixture gave two layers, each with a disperse phase when the inside of the tube in which the mixture was shaken was paraffined.

---

[1] Such reversals have been observed by Sanyal and Joshi, as previously cited, even in the presence of sodium oleate as emulsifier in concentrations as high as 0.075%.

The addition of a so-called emulsifying agent complicates not only the pulverization process but also the coagulation process, as before mentioned. It therefore does not seem safe to assume that the mechanics of dispersion can be preserved uniform for comparison purposes, with the use of various "emulsifying agents."

In the water series, we find oleic acid to reverse the phase relations with the alcohols, dimethyl aniline, nitrobenzene, and stanolax, and to more definitely cause carbon tetrachloride, benzene, and heptane to become dispersed in the water. The oleic acid did not completely prevent water from remaining dispersed in dimethyl aniline or nitrobenzene. In every case of the series, magnesium palmitate caused the water to become the dispersed phase. This fact suggests that the character of the film formed by the magnesium palmitate at the liquid-liquid interface is such as to protect water droplets in "oil," but not "oil" droplets in water, but the instability of oil droplets in water in the presence of magnesium palmitate is no more related to shapes and sizes of molecules than is instability of any other dispersed system in the presence of a coagulating agent.

In the glycerine series, potassium palmitate caused the phase relations to be reversed in every case, glycerine becoming the dispersion medium. In this case too, it is quite unlikely that the potassium palmitate had any marked influence upon the pulverization stage of *both* liquids (formation and disruption of lamellae), for neither the density or viscosity of the liquids or the mechanical treatment would be greatly modified. The interfacial tension, the property most changed, has a symmetrical influence upon the lamellae of both liquids and therefore has a minor influence upon the pulverization process. It only remains for the potassium palmitate to modify the relative rates of coagulation of the droplets of each phase. Empirically, it may be said that the droplets of "oil" in glycerine are stabilized or protected from coagulating, i. e., *fusing* upon encounter, whereas the droplets of glycerine in the oil are not so protected. This protection against "breaking" is usually assumed to be due to a film[1] of some kind at the interface. Although the nature and properties of this film are but vaguely understood, there seems to be no compelling reason for supposing it to consist of a simple monomolecular layer of oriented molecules, except, perhaps, when extremely small amounts of strongly polar-nonpolar stabilizers are used.[2] Even then there is no reason to believe that the *shapes and sizes* of the molecules are able to assert themselves in a mechanical or geometrical manner.

---

[1] Bancroft: J. Phys. Chem., 17, 514 (1913); "Applied Colloid Chemistry," (1921); Clayton: "Emulsions and Emulsification, (1923).

[2] Stamm: Third Colloid Symposium Monograph (1925).

Summary

A survey of recent studies of emulsions demonstrates that considerable of the original evidence for the "oriented wedge" theory of emulsions has not been confirmed and that the consequences predicted by the theory have not materialized. It is suggested that insufficient attention has been paid to the mechanism of emulsion formation. The formation of an emulsion by shaking, mixing, etc., may be safely considered as consisting of two stages—(1) a pulverization of both phases into lamellae and drops, and (2) a coagulation or reunion of the drops of one or both phases. The degree of dispersion (distribution of size of particle) and the phase relations of an emulsion are the net results of these two opposing processes. The function of an "emulsifying agent" is to more or less protect the drops of *one* phase already formed in the pulverizing stage from coagulating, while allowing the drops of the other phase to coagulate to give the dispersion medium. The protecting or stabilizing action is probably dependent upon the formation of a film at the interface. Although the character of such a stabilizing film is incompletely understood, it seems unlikely that the molecules in the film can determine the film properties by virtue of their *geometrical shape and size*, as suggested in the oriented wedge theory. Examples are given to demonstrate the complexity of the mechanism of emulsion formation.

NEW BOOKS .

The A B C of Atoms. *By Bertrand Russell. 20×14 cm pp. v + 162. New York: E. P. Dutton and Company, 1923. Price: $2.00.* The chapters are entitled: introductory; the periodic law; electrons and nuclei; the hydrogen spectrum; possible states of the hydrogen atom; the theory of quanta; refinements of the hydrogen spectrum; rings of electrons; X-rays; radio-activity; the structure of nuclei; the new physics and the wave theory of light; the new physics and relativity; Bohr's theory of the hydrogen spectrum.

There are a number of interesting passages in the book. "The chemical properties of the atom depend, almost entirely, upon the outer ring; so does the light that it emits, which is studied by the spectroscope. The inner rings of electrons give rise to X-rays when they are disturbed and it is chiefly by means of X-rays that their constitution is studied. The nucleus is the source of radio-activity. In radium and the other radio-active elements, the nucleus is unstable, and is apt to shoot out little particles with incredible speed," p. 6.

"One of the most astonishing things about the processes that take place in atoms is that they seem to be liable to sudden discontinuities, sudden jumps from one state of continuous motion to another. This motion of an electron round its nucleus seems to be like that of a flea, which crawls for a while, and then hops. The crawls proceed accurately according to the old laws of dynamics, but the hops are a new phenomenon, concerning which totally new laws have been discovered empirically, without any possibility (so far as can be seen) of connecting them with the old laws. There is a possibility that the old laws, which represented motion as a smooth continuous process, may be only statistical averages, and that, when we come down to a sufficiently minute scale, everything really proceeds by jumps, like the cinema, which produces a misleading appearance of continuous motion by means of a succession of separate pictures," p. 9.

"When I say that an electron has a certain amount of negative electricity, I mean merely that it behaves in a certain way. Electricity is not like red paint, a substance which can be put on to the electron and taken off again; it is merely a convenient name for certain physical laws," p. 25.

"It is impossible to get a ring to hold more than a certain number of electrons, though it has been suggested by Niels Bohr, in an extremely ingenious speculation, that a ring can hold more electrons when it has other rings outside it than when it is the outer ring. His theory accounts extraordinarily well for the peculiarities of the periodic table, and is therefore worth understanding, though it cannot yet be regarded as certainly true," p. 32.

"Sound-waves consist of vibrations of the air, or of whatever material medium is transmitting them, and cannot be propagated in a vacuum; whereas light-waves require no material medium. People have invented a medium, the aether, for the express purpose of transmitting light-waves. But all we really know is that the waves are transmitted; the aether is purely hypothetical, and does not really add anything to our knowledge. We know the mathematical properties of light-waves, and the sensations they produce when they reach the human eye, but we do not know what it is that undulates. We only suppose that something must undulate because we find it difficult to imagine waves otherwise," p. 41.

"All this so far is purely empirical. Rydberg's constant, and the formula for the lines of the hydrogen spectrum, were discovered merely by observation, and by hunting for some arithmetical formula which would make it possible to collect the different lines under some rule. For a long time the search failed because people employed wave-lengths instead of wave-numbers; the formulae are more complicated in wave-lengths, and therefore more difficult to discover empirically. Balmer, who discovered the formula for the visible lines in the hydrogen spectrum, expressed it in wave-lengths. But when expressed in this form it did not suggest Ritz's Principle of Combination, which led to the complete rule. Even after the rule was discovered, no one knew why there was such a rule, or what was the reason for the appearance of Rydberg's constant. The explanation of the rule, and the connection of Rydberg's constant with other known physical constants, was effected by Niels Bohr, whose theory will be explained in the next chapter," p. 48.

"It was obvious from the first that, when light is sent out by a body, this is due to something that goes on in the atom, but it used to be thought that, when the light is steady, whatever it is that causes the emission of light is going on all the time in all the atoms of the substance from which the light comes. The discovery that the lines of the spectrum are the differences between terms suggested to Bohr a quite different hypothesis, which proved immensely fruitful. He adopted the view that each of the terms corresponds to a stable condition of the atom, and that light is emitted when the atom passes from one stable state to another, and only then. The various lines of the spectrum are due, in this theory, to the various possible transitions between different stable stages. Each of the lines is a statistical phenomenon: a certain percentage of the atoms are making the transition that gives rise to this line. Some of the lines in the spectrum are very much brighter than others; these represent very common transitions, while the faint lines represent very rare ones. On a given occasion, some of the rarer possible transitions may not be occurring at all; in that case, the lines corresponding to these transitions will be wholly absent on this occasion," p. 49.

"Einstein's work has immense philosophical and theoretical importance, but the changes which it introduces in actual physics are very small indeed until we come to deal with velocities not much less than that of light. The new dynamics of the atom, on the contrary, not merely alters our theories, but alters our view as to what actually occurs, by leading to the conclusion that change is often discontinuous, and that most of the motions which should be possible are in fact impossible. This leaves us quite unable to account for the fact that all the motions that are in fact possible are exactly in accordance with the old principles, showing that the old principles, though incomplete, must be true up to a point. Having discovered that the old principles are not quite true, we are completely in the dark as to why they have as much truth as they evidently have. No doubt the solution of this puzzle will be found in time, but as yet there is not the faintest hint as to how the reconciliation can be effected," p. 57.

"A theory which explains all the known relevant facts down to the minutest particular may nevertheless be wrong. There may be other theories, which no one has yet thought of, which account equally well for all that is known. We cannot accept a theory with any confidence merely because it explains what is known. If we are to feel any security, we must be able to show that no other theory would account for the facts. Sometimes this is possible, but very often it is not. Poincaré advanced a proof that the facts of temperature radiation cannot be explained if we assume that radiation is a continuous process, and that any possible explanation must involve sudden jumps such as we have in the quantum theory. His argument is difficult, and it is possible that it may not ultimately prove wholly cogent. But it affords an instance of that further step without which scientific hypothesis must remain hypothetical," p. 79.

"Radio-activity is one of those processes of degeneration (in a certain technical sense) to which no converse process of regeneration is known. We see complex atoms breaking up, and it is natural to suppose that there are (or have been) circumstances under which they are put together out of simpler atoms. But no trace of any such circumstances has been discovered. In this respect, as in some others, the universe *seems* like a clock running down, with no mechanism for winding it up again. All the uranium in the world is breaking down, and we know of no source from which new uranium can come. Under these circumstances it seems strange that there should be any uranium. But if, like some insects, we lived only for a single spring day, we should think it strange that there should be any ice in the world, since we should find it always melting and never being formed. Perhaps the universe has long cycles of alternate winding-up and running-down; if so, we are in the part of the cycle in which the universe (or at least our portion of it) runs down. Everything pleasant is associated with this running down, because it is only this process that liberates energy for the purposes that we regard as useful. It is time, however, to return from these speculations to the mechanism of radio-activity," p. 112.

"The fact that the atomic weights are whole numbers, together with the facts of radioactivity and of Rutherford's bombardment, lead irresistibly to the conclusion that the weight of an atom is due to helium nuclei and hydrogen nuclei which exist together in its nucleus. The over-crowding in the nucleus of a heavy atom must be something fearful. Radium C, which emits the α-particles that Rutherford used in his experiments, has a nucleus whose radius is about three million-millionths of a centimetre (about one million-millionth of an inch). Its atomic number is 83 and its atomic weight is 214. This means that in this tiny space it must contain 53 helium nuclei and 2 hydrogen nuceli; it must also (as we shall see in a moment) contain 131 electrons. It is no wonder that helium nuclei and electrons move fast when radio-activity liberates them from this slum," p. 127.

"In the physics of the atom, as it has become in modern times, everything is atomic, and there are sudden jumps from one condition to another. The electron and the hydrogen nucleus are the true "afoms" both of electricity and of matter. According to the quantum theory, there are also atomic quantities, not of energy as was thought when the theory was first suggested, but of what is called "action." The word "action," in physics, has a precise technical meaning; it may be regarded as the result of energy operating for a certain time. Thus if a given amount of energy operates for two seconds, there is twice as much action as if it operated for one second; if it operates for a minute, there is 60 times as much action, and so on. If twice the amount of energy operates for a second, there is again twice as much action, and so on. If the energy which is operating is variable, and we wish to estimate its action during a given time, we divide the time into a number of little bits, during each of which the energy will vary so little that it may be regarded as constant; we then multiply the energy during each little interval of time by the length of the interval, and add up for all the intervals. As we make the intervals smaller and more numerous, the result of our addition approaches nearer and nearer to a certain limit; this limit we define as the total action during the total period of time concerned. Action is a very important conception in physics; from the point of view of theory it is more important than energy, which has been deposed from its eminence by the theory of relativity. Planck's quantum h is of the nature of action; thus the quantum theory amounts to saying that there are atoms of action," p. 134.

"It must be confessed that the quantum principle in its modern form is far more astonishing and bewildering than is its older form. It might have seemed odd that energy should exist in little indivisible parcels, but at any rate it was an idea that could be grasped. But in the modern form of the principle, nothing is said, in the first instance, about what is going on at a given moment, or about atoms of energy existing at all times, but only about the total result of a process that takes time. Every periodic process arranges itself so as to have achieved a certain amount by the time one period is completed. This seems to show that nature has a kind of foresight, and also knows the integral calculus, without which it is impossible to know how fast to go at each instant so as to achieve a certain result in the end. All this sounds incredible. No doubt the fact is that the principle has assumed a complicated form because it has forced its way through, owing to experimental evidence, in a science built upon totally different notions. The revolution in physical notions introduced by Einstein has as yet by no means produced its full effect. When it has, it is probable that the quantum principle will take on some simple and easily intelligible form," p. 139.

"The theory of relativity has shown that most of traditional dynamics, which was supposed to contain scientific laws, really consisted of conventions as to measurement, and was strictly analogous to the "great law" that there are always three feet to a yard. In particular, this applies to the conservation of energy. This makes it plausible to suppose that every apparent law of nature which strikes us as reasonable is not really a law of nature, but a concealed convention, plastered on to nature by our love of what we, in our arrogance, choose to consider rational. Eddington hints that a real law of nature is likely to stand out by the fact that it appears to us irrational, since in that case it is less likely that we have invented it to satisfy our intellectual taste. And from this point of view he inclines to the belief that the quantum-principle is the first real law of nature that has been discovered in physics," p. 158.

Wilder D. Bancroft

Regeneration. *By Jacques Loeb. 24×16 cm; pp. 143 New York and London: McGraw-Hill Book Company, 1924 Price: $2.00.* The final revision of this book was finished by Loeb just before his death. The first part deals with mutilation and regeneration, and the chapters are entitled: introduction; general remarks about the material and the experiments; regeneration and mass relation in isolated leaves of *Bryophyllum*; the inhibiting action of the rapidly growing notches on the other notches of a leaf; the influence of gravity on the formation of roots and shoots in a detached leaf of *Bryophyllum*; why does separation of a leaf from the plant induce the growth of roots and shoots in a leaf?; the validity of the mass relation for regeneration in a defoliated piece of stem of *Bryophyllum calycinum*; the rôle of the inhibiting effect of rapidly growing parts in the regeneration of the stem.

The second part deals with polarity in regeneration, and the chapters are entitled: the influence of the leaf on the regeneration in the stem; the influence of gravity on the polar character of regeneration in a stem of *Bryophyllum* (2); the inhibitory action of apical leaves on the formation of shoots in the lower part of the stem; callus formation; inhibitory effects of a second order by an apical leaf; the inhibitory effect of an apical leaf on shoot formation in a stem suspended horizontally; the growth of the axillary shoots; some preliminary experiments on the path of the ascending and descending sap in the stem of *Bryophyllum*; concluding remarks.

"About a generation ago biologists devoted considerable time to a discussion of the vitalistic and mechanistic conception of life processes. The impulse for this discussion was given at that time by the experiments of Roux and of Driesch upon the development of eggs, parts of which had been destroyed or removed in the first stages of segmentation. It was generally or frequently observed that the development of the mutilated egg resulted in the formation of a normal organism. Driesch maintained that this phenomenon could not be adequately explained on a purely physico-chemical basis, but that in addition a metaphysical guiding principle inherent in the organism as a whole was to be postulated. The opposite view was held by Roux. The controversy was never settled, for the simple reason that on account of the microscopic size of the egg cells the experiments of both authors had to be purely qualitative. An adequate explanation of natural phenomena is possible only on the basis of quantitative experiments and such an explanation consists in the derivation of the results from a rationalistic mathematical formula (a so-called "law") without the introduction of arbitrary constants," p. v.

"The writer has for a number of years conducted quantitative experiments on the regeneration of a plant, *Bryophyllum calycinum*, which have made it possible to correlate the process of regeneration with the quantity of chemical material. By comparing the dry weight of the regenerated shoots and roots with the dry weight of the leaves or stems which were used for regeneration, it could be shown that in the presence of light the quantity of regeneration was under equal conditions of illumination, temperature, and in equal time in direct proportion to the mass of the leaves of stems from which regeneration started. If we make the legitimate assumption that the material required for the formation of new shoots or roots was under the conditions of our experiments produced by the chlorophyll contained in the leaf or stem, it follows that the quantity of regeneration is determined in this case by the mass of material available in the stem or leaf for synthetic processes. Under the guidance of this mass relation (which may be, in part at least, identical with the law of mass action), it could be shown that mutilation of the plant leads to a collection of sap in places where it would not have collected without the mutilation. This accounts for the fact that mutilation leads to growth in places of the organism where no growth would have occurred without mutilation. The process of regeneration was thus revealed as a purely physico-chemical phenomenon, leaving no necessity nor room for the postulation of a guiding principle aside from the purely physico-chemical forces," p. vi.

"It requires several weeks for a leaf or stem to produce new shoots and roots of sufficient quantity to permit exact weighings. If the time allowed for regeneration is too short, so that the roots and shoots are too small, the error made in cutting off the roots and shoots becomes considerable, since it is not possible to cut off these organs at their base with absolute accuracy. On the other hand, when the shoots reach a considerable size, they participate to an increasing degree in the assimilation. As long as their assimilating mass is small compared with the assimilating mass of the leaf on which they grow, the error committed in neglecting this influence is small; if necessary it can be corrected by deducting the mass of the shoots from that of the leaf in calculating the influence of the active mass of the leaf on the production of roots or shoots. The writer carried on his experiments for about three or four weeks; in this time the mass of roots and shoots produced under the conditions of temperature and light prevailing in the greenhouse was sufficiently large to make the error committed in cutting off the roots and shoots comparatively small. In order to rule out accidental variations, each experiment was made on a larger number of leaves or stems, rarely fewer than six in one experiment," p. 10.

"It is obvious that the leaves suspended in air form a much smaller quantity of dry weight of shoots and roots per gram of dry weight of leaf during the same time and under the same conditions than the leaves dipping into water. Hence, if we accelerate the growth of some notches in the leaf, *e. g.*, by dipping them into water, we thereby inhibit the growth in the other notches.

"When leaves are suspended entirely and permanently in air, practically all the notches commence to form shoots and roots, but not all will continue to grow. Some notches will grow more rapidly than others and all the material will flow to the more rapidly growing notches. This explains why ultimately only a limited number of notches will continue to grow in air, usually in the more fleshy parts of the leaf.

"The fact that the sap available in a leaf flows to those notches where the growth is most rapid can be seen directly in leaves which form a purplish pigment (probably anthocyanin). This occurs only in leaves of *Bryophyllum* suspended in air, not in leaves which dip into water," p. 22.

"We now understand why the leaf of *Bryophyllum calycinum*, when it is detached from the plant, forms shoots and roots in its notches while this regeneration is inhibited when the leaf forms part of a normal plant. The leaf connected with a normal plant can be dipped into water without forming roots or shoots in its notches. All the material which might be available for shoot and root formation in the leaf is sent into the stem. During a recent visit in Bermuda, I have had a chance to examine thousands of plants of *Bryophyllum calycinum* without finding a single case where a leaf connected with a plant had formed roots or shoots. The same has been true in my greenhouse, and only recently have I had an opportunity to observe about six plants, the older leaves of which formed some tiny shoots. The plants in which this occurred were old and in two boxes containing no other plants; so that the suspicion is justified that their roots had suffered some common injury or disease. When a stem contains many leaves, and when the growth of the stem is stopped or when the sap flow has suffered, it is possible that shoots and roots may originate on leaves still connected with the stem. All that is needed for such growth is that the flow of material from the leaf into the stem should be partially or completely prevented," p. 41.

"It is the purpose of this little volume to show that a simple mass relation can be used as a guide through the bewildering maze of the phenomena of regeneration. This mass relation states that equal masses of isolated sister leaves produce, under equal conditions of illumination, temperature, etc., approximately equal masses of shoots and roots in equal time. With this relation it was possible to explain why isolation of a leaf leads to regeneration; namely, because the material available in the leaf for growth flows normally into the stem where it is used for the growth of roots, shoots, and of the stem itself. When a piece of stem inhibits the regeneration in a leaf the stem gains in dry weight to an amount equal to the diminution in the dry weight of shoots and roots in the leaf due to the stem. It was shown that this mass relation holds also for the the formation of roots and shoots in an isolated piece of the stem. Equal masses of stems produce under equal conditions of illumination, temperature, etc., approximately equal masses of roots and shoots in equal time.

"In both cases a second physiological factor was revealed which must be considered; namely, that the flow of sap in a leaf or stem is secondarily directed towards that part of a leaf or stem where the more rapid growth of shoots or roots occurs. This explains why only some but not all of the anlagen for roots or shoots in a leaf or stem will persist in growing out; while the growth of the others will stop. This again would have remained merely a hypothesis had it not been possible to prove it quantitatively on the basis of the mass relation.

"A further complication arises in the fact of the polar character of the regeneration of roots and shoots in the stem of *Bryophyllum*. Two possibilities presented themselves for the explanation of this phenomenon: the polar character of the regeneration in the stem is either due to a difference in the chemical character of the ascending and descending sap or to a difference in the nature of the cells or anlagen which are primarily reached by the ascending and descending sap. It was possible to decide between the two hypotheses by using the mass relation, inasmuch as it could be shown that the shoots and roots formed in a piece of stem, increase with the mass of the leaf attached to the stem. Since the sap in the leaf forms shoots and roots in the same notch when the anlagen for these two organs exist closely together, the fact that shoots are formed at one and roots at the other end of a stem indicates that the ascending and descending sap of a leaf reach primarily different anlagen, and this conclusion was corroborated by two groups of facts; first, by directing with the aid of gravity the ascending sap in a stem to the tissues capable of root formation roots were produced in abundance by the ascending sap; and second, the mass of shoots produced in the basal part of the stem increased with the mass of an apical leaf. These facts seem to eliminate the idea that the polar character of regeneration is due to any chemical differences between the ascending and descending sap although such differences exist.

"The fact that certain mysterious substances like the "vitamines" or "hormones" may accelerate the rate of growth of an organ and consequently perhaps also the rate of regeneration, is neither in contradiction with the mass relation nor with its application to phenomena or regeneration. The sap sent out by a leaf contains probably all the substances needed for growth, inclusive also of "vitamines" and "hormones."

"It is quite probable that the principle of mass relation can serve as a guide in phenomena of regeneration in other organisms than *Bryophyllum*. In order to apply the principle we must be able to measure with a certain degree of accuracy the quantity of the material available for the synthetic processes underlying regeneration. This is possible in plants where the leaf is the main organ for the production of this material and where the light is the main source of energy for its production. It is also possible where we deal with definite quantities of stored material, as *e. g.*, in a potato, and where therefore the quantity of the mass of material available for regeneration can be varied at will. Unfortunately it is not easy to control the mass of available material for regeneration in animals. The material from which new organs are regenerated in animals must be furnished either by the food taken up or by the hydrolysis of material in the cells of the animal. All attempts to arrive at a rationalistic theory of regeneration in animals will have to rely on the use of organisms where the mass of material available for regeneration can be controlled as easily as in *Bryophyllum*," p. 141.

Wilder D. Bancroft

The States of Aggregation. *By Gustav Tammann. Translated by R. F. Mehl. 22×15 cm; pp. xi + 297. New York: D. Van Nostrand Company, 1925. Price: $5.00.* This is a welcome translation from the second German edition of Tammann's well-known book. The chapters are entitled: the states of aggregation; the equilibria of the states of aggregation; equilibria between vapor and liquid; the equilibrium curves; the melting curve; polymorphism; the phase diagram; the deformation of crystals and its consequences; the transition of an unstable into a stable state of aggregation; liquid crystals.

Boric anhydride appears to be a substance which does not crystallize at any temperature under atmospheric pressure, p. 38. With increasing pressure the melting-points of the tertiary alcohols are said to pass through a maximum, p. 96. From the pressure-temperature curves for the different modifications of ice, the author considers it possible that they may be isomers with a molecular weight of 54, p. 148.

"It is a fact worthy of notice that in some cases an expected transition will not occur, or will occur very irregularly, under ordinary conditions, but that in the presence of some medium the transition will take place promptly and completely. Such a case in the transition of ordinary tin into grey tin (transition point 20°) which ordinarily occurs very irregularly and with a great amount of supercooling. In contact with a solution of $SnCl_4$ the transition is regular, though requiring a good length of time for completion. Evidently the number of transition centers on the surface of the tin is greatly increased by the medium.

"The influence of dissolved admixture upon the transition point is also of interest. The crystal Hg_5Tl_2, m. p. 14.4°, in the pure state shows no transition point. An addition of 0.0038 percent Pb causes the appearance of a very significant transition point upon the cooling curve at 12-13°, accompanied by a discontinuous change in volume," p. 124.

"The blue earth in which diamonds are found imbedded may have worked up as olivine from a depth of 20-30 km., corresponding to a pressure of 6000-9000 kg./cm.$_2$ and a temperature of 1300°-1500°. Rapid cooling to 1000° could have produced the diamond as such But there still remains a degree of uncertainty about the matter, for the beginning of the formation of graphite in diamond at 1000°C. is distinct after a period of twenty-four hours, whereas the half-liquid magma must have maintained a temperature above 1000° for a period considerably greater than twenty-four hours after the pressure had fallen to small values, and yet no paramorphs of graphite or of diamond have been found in the blue earth. Laboratory experience has shown that the important factor in the production of a new crystalline form is the temperature to which the original crystalline form is allowed to fall. At a definite temperature, in the course of the cooling, the number of crystallization centers increases very greatly, and in view of this fact it may be seen that a diamond crystal that had been once cooled would be much less stable at a temperature of 1300°-1500° than one that had never been permitted to cool.

"With respect to the artificial preparation of diamond it may be said that the transformation velocity of diamond decreases rapidly with the temperature upon a steep transformation curve, as, for example, upon the transformation curve of Ice I into Ice II. Experimental difficulties are multiplied by the fact that cylinders made of material with the greatest strength at high temperatures are likely to expand so greatly at a temperature of 1000° with pressure as low as 3000 kg. that the desired pressure rise of 6000-10,000 kg. becomes impracticable. Whether or not the transformation velocity of graphite into diamond at 1000° is noticeable cannot be said. At best such an artificial production of diamond would produce no large crystals but only a fine-grained crystalline conglomerate which could find use as an abrasive," p. 185.

"If a slowly increasing force be allowed to work upon a cube cut from a plastic crystalline conglomerate, such as copper, there will be seen upon microscopic investigation of the polished plane of the crystal parallel to the direction of pressure, fine, dark, parallel lines, in the individual crystallites. These gliding-lines are the traces of gliding-planes upon which the portions of each crystallite are displaced with respect to each other, and are so oriented to the direction of pressure that they exert a minimum of resistance to permanent deformation. The pressure at which the gliding-lines appear corresponds to the elastic limit, which may be exactly determined in this way. The elastic limit obtained for the operation of a pressure agrees with that found upon the application of tension. If the pressure be raised further, these gliding-lines appear in other crystallites, and with increasing pressure the angle of the gliding-line with the direction of pressure becomes sharper, and finally new sets of gliding-lines appear in the crystallites, intersecting the original set of parallel lines.

"The explanation of the fact that the gliding-planes do not form in all crystallites at the same pressure (with copper the first gliding-lines appear at 203 kg./cm.$_2$, and the last at 2000 kg./cm..) lies in the fact that the force at which gliding takes place in a crystal depends in great degree upon the orientation of the crystallites with respect to the direction of the force.

"Accordingly, all crystallites are finally divided by several systems of gliding-planes, and in this condition each crystallite can endure further deformations of a much greater magnitude. The piece, now divided into numberless small elements—as high as 1000 to

1,000,000 elements have been counted in a single crystallite—has obtained the ability to flow. With copper, the pressure at which flow begins, lies at about 2780 kg./cm.., and therefore exceeds the elastic limit thirtyfold." p. 200.

"Cold work upon a piece of metal causes the formation of laminated fragments to take place within the metal. With sufficient temperature increase very small, new crystallites appear at the boundaries of the laminated fragments, and these new crystallites increase in size until finally the whole piece consists of well-developed grains. Corresponding to the structural changes there also occur changes in the physical and chemical properties of the metal. In metallography this process is termed *recrystallization*. A somewhat similar process takes place in the union of the particles of amorphous bodies, and in the combination of liquid droplets to larger drops, but between the agglomeration or coalescence of isotropic particles and the union of anisotropic particles, a difference exists with respect both to the beginning of the process and to the structure of the end-product. At the beginning of the combination of anisotropic fragments there are formed, as has been shown with iron and copper, minute new grains at the boundaries of the fragments, whereas in the combination of amorphous fragments the process consists merely in a combination of two or more grains into a larger grain. The end-product of recrystallization is a crystalline conglomerate, the crystallites of which are separated from each other either by voids or by layers of varying thickness made up of non-isomorphous admixtures, whereas the combination of isotropic surfaces of the same composition leads to a physically homogeneous mass.

"The process of recrystallization plays a dominant rôle in many geological processes, such as the formation of glaciers, the production of marble from limestone, and the formation of crystalline schists. The process is of importance in the technology, not only of metallography, but also of ceramics. Unfortunately the workers in fields differing so much as these have little opportunity for the exchange of observations, and the valuable facts known to the one group have often remained unknown to the other," p. 205.

"The weight of many layers of snow deposited upon glaciers causes the snow crystals to form a grain-like glacier ice. In time this coarsely crystalline aggregate becomes clear, and in the coarse of years the size and character of the grains alter considerably. Accordingly, the undermost ice at the end of the glacier is made up of grains quite different from the grains formed first. Besides the grains of the sizes of a pin-head and a hazel-nut present in old glacier ice, there are frequently found gigantic grains 10 cm. in diameter. The grain-like structure of artificial ice of the clear glacial ice formed first upon the compression of the snow crystals is quite easily seen, especially when the grains in the ice are displaced relatively to one another by compression. In the new glacier ice the grains are generally irregularly oriented with respect to one another. In time, however, in addition to the growth of the grains, a re-orientation takes place so that in large masses of ice all of the grains have parallel optical axes. Investigation of this at different points upon Alpine glaciers has given different results with respect to the spreading of the sphere of similar grain orientation. E. v. Drygalski observed in old inland ice and in the deeper layers of icebergs of the antarctic the presence of grains varying in size from that of a pinhead to that of a hazel nut, which were optically similarly oriented," p. 217.

Tammann notes, p. 235, that a beautiful blue glass can be obtained by a suitable heating of difficulty fusible Jena glass. Since he does not add a black background, he has no real conception how beautiful these blues may be.

"If a liquid consist of two or more kinds of molecules, polymers, or isomers, and if the equilibrium between these molecules be dependent upon the temperature, the crystallization velocity can then be independent of the temperature only in the case where the equilibrium characteristic to the melting-point produces itself very rapidly, when the liquid is warmed to the temperature of the melting point," p. 270.

On p. 290 is the statement that the bright colors observed when cholesterol esters solidify slowly depend on the size of the spherulites suspended in the melt. This is inaccurate. The colors are a Christiansen effect and vary with the temperature.

Wilder D. Bancroft

A RELATIONSHIP BETWEEN ATOMIC NUMBERS AND THE PROPERTIES OF IONS IN THE CRYSTAL LATTICE*

III. The Metallic State—A Preliminary Study

BY ARTHUR F. SCOTT

The fundamental principle known as the Periodic Law carries the implication that the chemical characteristics of the elements are reflected in the physical properties of the solid state. The significance of this implication becomes more definite if it may be restated as follows: The physical properties of the elements in the solid state, say, the atomic volumes, are controlled by the identical factors that control the chemical behavior of the elements. Obviously, if we had a precise expression of this generalization, we should have information of value to our understanding both of chemical phenomena and of the crystalline state. But to demonstrate this assumption would necessitate not only a detailed knowledge of the structure of complex atoms but also a rather complete theory of the solid, metallic state. Both of these requisites, unfortunately, are wanting. Nevertheless it may be hoped that the general theory of the atom as developed by Bohr as well as the picture of the crystalline state afforded by X-ray analysis, will furnish a basis for a preliminary analysis of the problem, yielding, at the best, empirical results. Two attempts along these lines have already been made by the author, and the present study is a continuation of them. For the sake of simplicity the present analysis will be confined to the spatial distribution of atoms, which may be taken as typical of the physical properties of elements in the solid state.

In taking up this study it will be convenient to restrict ourselves at the outset to those elements whose ions have electronic structures similar to the corresponding inert gases and which form crystals of the so-called metallic nature. Furthermore, before starting out on an investigation of this limited and relatively simple group of elements, it will be necessary to formulate some concept of the metallic state. For this purpose we shall make certain postulates which, we have sufficient reasons for believing, are not incompatible with the actual conditions. We shall assume that metals consist of ions and "free" electrons, the latter being what we ordinarily consider valence electrons. The ions are bound together by electrostatic forces and are repelled by forces which are not purely electrostatic in nature. We may easily believe that the positions which the ions take in the crystal lattice and even the type of lattice depend in general on the action of these two forces. Hence, if we are to search for the determining factor of the lattice distance, we must discover the law of force which describes the net effect of these attractive and repellent forces. But this law of force is unknown; and further an understanding of the exact nature of the two forces of which it is a composite is complicated by several factors of which we shall mention two which are very important. First, the repellent force is without doubt closely associated with the electronic structure of the ion and of this relationship atomic theory has thus far offered us no satisfactory explanation. And second, these forces cannot be separated from their dependence on the "free", valence electrons, concerning which we have no accepted hypothesis when they are in the crystal lattice. If, therefore, a knowledge of these two factors is vital to an understanding of the spatial properties of lattice structures, we may commence our analysis with an examination of the scant data available concerning them.

---

* Contribution from the Department of Chemistry of Reed College.

Regarding the ions themselves we have very little quantitative information. The elaborate theory of Bohr gives us a fairly good idea as to what quantum orbits the electrons occupy in the various ions. Our information does not go far enough, however, to give us the diameters of these ions, or rather of the orbits of the outermost electrons. If we take the distance from the center of the ion to the outermost point through which an electron passes, we may assume this distance to be the radius of domain of the ion, or conversely, if we know the radius of this domain we may assume that we have some measure of the extreme orbits of an ion. Some such arbitrary definition of ionic dimensions is necessary if we are to consider the atom to be a dynamical system. Now, Grimm[1] has computed the radii of domain of a number of ions after a method suggested by Fajans and Herzfeld,[2] and we may employ his data (Table I) to give us an idea as to the size of the orbits.

TABLE I

Ionic Radii and Values of f

Valence	− −	−	o	+	++	+++	++++
			He	Li	Be	B	C
$f\times10^6$			2.32	5.8	12.9	23.2	38.6
	O	F	Ne	Na	Mg	Al	Si
$r\times10^8$ cm.	0.89	0.75	0.63	0.52	0.39		
$f\times10^6$	0.66	1.85	4.63	9.27	16.0	27.3	46.3
	S	Cl	A	K	Ca	Sc	Ti
$r\times10^8$ cm.	1.09	0.95	0.87	0.79	0.67		
$r\times10^6$	0.31	0.53	1.10	2.08	3.43	4.78	6.72
	Se	Br	Kr	Rb	Sr	Y	Zr
$r\times10^8$ cm.	1.15	1.02	0.97	0.91	0.87		
$f\times10^6$	0.28	0.38	0.73	1.29	2.06	1.78	2.28
	Te	I	Xe	Cs	Ba	La	Ce
$r\times10^8$ cm.	1.24	1.12	1.10	1.07	1.07		
$f\times10^6$	0.19	0.25	0.445	0.74	1.08	1.16	1.52
			Zn^{++}	Cd^{++}			
$f\times10^6$			16.0	1.90			

---

[1] Grimm: Z. physik. Chem., **98**, 353 (1921).

[2] Fajans and Herzfeld: Z. Physik, **2**, 309 (1920).

It should be noted, however, that Grimm's figures have no validity as absolute values and are probably too small because of the simplifying assumptions on which they are based; but there is considerable support for their relative magnitudes. One fact is obvious from these data: For a series of iso-electronic[1] ions the radius decreases with increasing nuclear charge, the atomic number.

If we are going to interpret this information by imagining the decrease in the domain of an ion with increase in nuclear charge to be brought about by a tightening of the electronic orbits about the nucleus, we must also believe the electrons in these orbits to be bound more and more firmly. As a measure of the firmness with which an electron is held in its orbit, we have the constraint, *f*, which is the restoring force when an electron suffers a displacement of one centimetre, assuming the force to be proportional to the displacement. Although this assumption would doubtless be incorrect for displacements of so great a magnitude as one centimetre, we may safely assume that it is true for the small displacements which do occur.

Smyth[2] has shown how this constraint may be calculated from the refractive index of the ions according to the formula:

$$f = \frac{4\pi N_0 n e^2}{3M_\infty} \tag{1}$$

in which N_0 is Avogadro's number, 6.061×10^{23}; n is the number of displaceable electrons per ion; e is the electronic charge; and M_∞ is the molecular refraction for light of infinite wave-length. By making use of the data for the molecular refraction for the D-line of the individual ions obtained by Fajans and Joos, and Wasastjerna, Smyth has computed *f* for various ions. These values are included in Table I. "In calculating *f*," says Smyth, "it was assumed that all the electrons in the outer layer of the atom or those whose orbits extended farthest out from the nucleus were capable of suffering displacement and thus contributing to the refraction, the others being too rigidly bound to have an appreciable effect upon the refraction." In spite of the fact that the values for *f* presented in Table I are sufficiently accurate for the purpose they will serve, it must, nevertheless, be pointed out that the ingenious method employed in this determination of the refractivities of individual ions introduces certain errors which limit their validity.

A scrutiny of the data in Table I shows at once that in a series of iso-electronic ions the constraint increases as the radius decreases, which is the expected result. Moreover since both of these quantities depend ultimately upon the effective nuclear charge, it is only natural to expect some definite connection to exist between them. What this relationship is, will appear later when the subject has been examined a little more thoroughly.

Inasmuch as the constraint factor will subsequently be shown to be of considerable significance in the theory of the crystalline state, it is advisable to investigate its relationship to the effective nuclear charge more completely. The dependence of the constraint on the nuclear charge seems to follow a uniform rule. For illustrative purpose, let us take as a typical case the effect of an increase in the atomic number upon the constraints of the iso-electronic ions of the first period and compare this effect to that produced in the iso-electronic ions of the second period. If to begin with we compare the constraints on the outer group of electrons in helium with those of neon, we should naturally expect to find a difference, first, because of the difference in nuclear charge, and second, because of the screening effect in the second case. Now, if the increase in nuclear charge affects both series of ions to the same degree, we should expect corresponding ions, say, lithium and sodium, to have their constraints in the same ratio as the constraints in helium and neon. Furthermore we should expect the same rule to hold for the other series of iso-electronic ions under discussion. That this interpretation is probably the correct one can be shown by plotting the constraints of the different series of iso-electronic ions against one basic series. In doing so, however, the limitations in the accuracy of the data made it impossible to decide whether the constraint or the square-root of the constraint was proper for such a comparison. In the course of this paper substantial grounds will be indicated for the choice of the latter function. Also, because of the convenience in plotting, the square-root of the constraint was selected and the values of f for the iso-electronic series of ions of the neon-type were chosen to be the determinant points on the abscissa. This rather arbitrary procedure has no effect whatever upon the interpretation which has been presented above, which essentially is that the effective nuclear charge affects the constraints acting on the electrons in the outer group in any series of iso-electronic ions in a uniform manner. No more formal statement of this relationship is possible or necessary for our purpose at this time.

---

[1] We shall use the term, iso-electronic, to signify ions with the same electronic structure; e.g., He—Li—Be—B—C.

[2] Smyth: Phil. Mag., 50, 361 (1925).

The results obtained by means of the foregoing scheme are portrayed in Fig. 1. Only a few observations need be made on this diagram. We could obviously attempt to approximate constraint values for some of the ions that are not given, such as P^+, etc., but this is scarcely justifiable in view of the known uncertainty of the data. And for the same reasons it does not seem advisable to conjecture regarding the significance to be attached to the juncture of the lines at point a. One alteration may nevertheless be suggested. The abnormally small values for scandium and titanium and the similar abnormality appearing in the points of the corresponding elements of the following periods may be taken as following in a general sense the predictions of the Bohr theory. But there is no obvious reason why the line though the points Sr—Y—Zr should show such a marked deviation from the behavior of the two adjacent lines. If we accept this conclusion, it is possible to draw a line, such as the dotted line, which would be free from this objection. From this line we may then interpolate new values of f for Y and Zr, which hereafter we will designate as the hypothetical values.

We may adduce some further evidence to corroborate the above interpretation if we reverse the procedure used in Fig. 1. Take, for instance, the alkali metals. The differences in the constraints of these ions have been attributed to differences in the structures of the ions and also to differences in the effective nuclear charges. Our premise so far has been that an increase or a decrease in the nuclear charge affects the constraint of each type of ion uniformly. Hence, if we were to plot against the constraint values for the alkali metals the constraints of the alkaline earth metals, where the nuclear charge has been increased by one, we should expect the latter values to be related to the former by some linear function. This has been done in Fig. 2

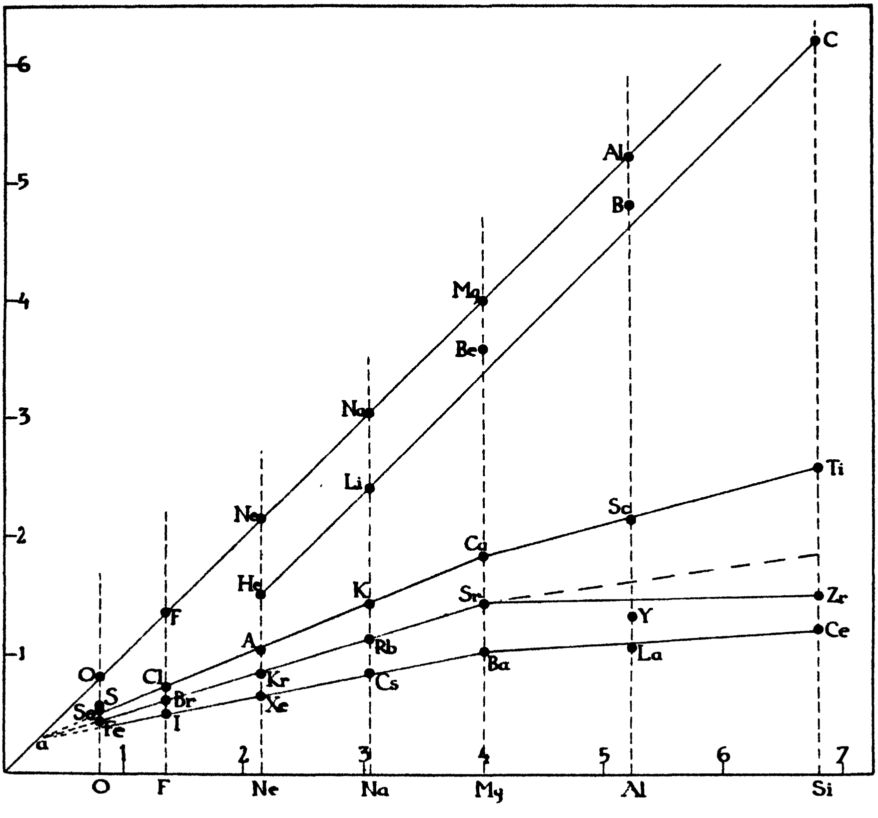


FIG. 1

Square-root of Constraint of Series of Iso-electronic Ions plotted against Square-root of Constraint of Ions of Second Period.

where the elements portrayed in Fig. 1 are plotted in this new manner, again using the square-root of the constraint. Here we find our expectations fulfilled, even to the predicted inaccuracy of the points for Y and Zr. In the present case as well as in the case to come up later, these hypothetical values (indicated by crosses in circles) obtained from Fig. 1 are found to be satisfactory. Inherent in the mode of plotting employed in both of these figures is the difficulty that if one of the abscissa points is in error, this error re-appears in all of the points plotted against it. For instance, an error in the constraint value of oxygen in Fig. 1 could be held largely responsible for the

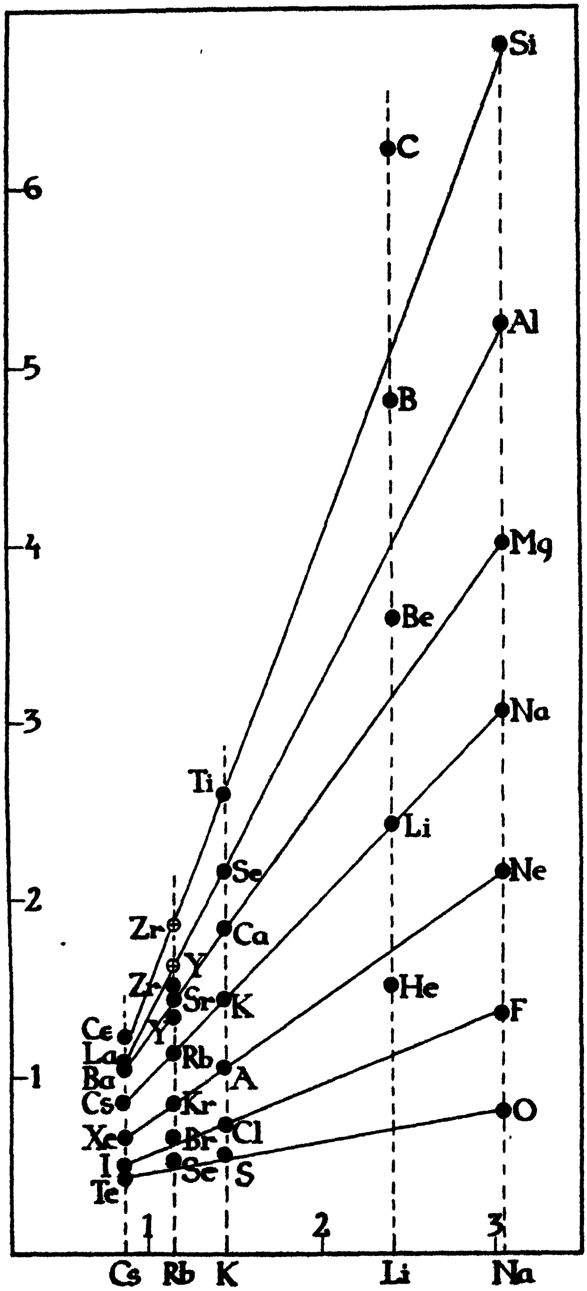


Fig. 2

Square-root of Constraint of Different Groups of Elements plotted against Square-root of Constraint of Alkali Metals.

discrepancies exhibited by the points plotted against it. Likewise, if in the same figure the silicon value were smaller, the agreement shown by the elements of the first period would be greatly improved. Again, in Fig. 2 if we could maintain that the helium point should come on the line through the points of the inert gases, the vertical line for the first period would be shifted to the left; and the point for beryllium would fall on the line of the third group elements and the boron point would come almost on the line of the fourth group elements. These last two cases are strongly suggestive of an analogous relationship well known in chemistry. But other assumptions would bring about the same results. For this reason it is easy to see the futility of attempting to reconstruct the two figures along hypothetically correct lines. Another observation which should not be ignored is the abnormal position of the points for the elements of the first period. The explanation of their unique and abnormal behavior must be sought in the great difference in the structure of these ions compared to that of ions in the other periods. It should be noted, however, that the constraints on the two electrons in this series of iso-electronic ions follow the same rule in respect to the atomic number as do the constraints in the other series of ions. Finally, from the satisfactory nature of the agreement shown in both of these figures, we may conclude that whatever the law of force is which controls the electrons in the outer group of an ion, it appears to be the same for any series of iso-electronic ions.

It has already been emphasized that the radius of domain of the ion and the constraint on the ionic electrons are both similarly dependent on the nuclear charge of the ion. Even though the exact relation is unknown in the former case just as in the second, we should naturally expect the radii to be capable of the same mode of treatment as we have used for the constraints in the first two figures. As a matter of fact they exhibit unmistakably the same characteristics. Nevertheless, corresponding representations are not given because they would not add materially to the foregoing statement, and for the further reason that the data are limited and only approximate.

Since there is no evidence to the contrary, we are justified in assuming that these two properties of ions, viz., the constraint and radius of domain, remain unaltered and follow identical rules irrespective of whether they are in solution, in the gaseous state, or in the solid state, so long as they are not subjected to any disturbing forces. But such a condition obviously cannot be realized in the crystal; for each ion must be affected to some degree by the ions which surround it and the presence of the valence electrons must likewise be of some consequence. If now we disregard the mutual influence of the ions themselves, we may obtain some information concerning the effect of the valence electrons upon the electrons in the ion by a consideration of the atom in the gaseous state. Here we have merely the atom consisting of the ion surrounded by the valence electrons. In such a case, as Compton[1] has pointed out, there is an attraction rather than a repulsion acting on the valence electron; and this attraction results from a distortion of the electronic shell of the ion in the field of the valence electron. In short, we see that the valence electron, although it has its own unique quantum orbit, is influenced to a certain extent by the outer group of electrons in an ion and vice versa. It is inconceivable that these influences should vanish completely when the atoms come together in a crystal lattice. A knowledge might be gained of the relationship existing between such a property as the constraint on the ionic electrons, on the one hand, and on the valence electrons, on the other, when the atom is isolated in the gaseous state. But this knowledge would be of little assistance in a study of the atom in the solid state because this latter relationship would probably be seriously modified by the added influence of the surrounding atoms.

---

[1] Compton: Science, 63, 53 (1926).

Nevertheless, in spite of the complications introduced by the neighboring atoms, we may still expect to find some relationship between the ionic electrons and the valence electrons. Let us therefore test the suggested relationship between the constraints of these two groups of electrons. For this purpose, in addition to the data already presented in Table I for the constraints on the electrons in the outer group, we shall require values for the constraints on the valence electrons in the crystal lattice. To obtain these we need only accept Haber's "square-root" rule,[1] which is usually written:

$$\nu_v/\nu_r = \sqrt{M/m} \qquad (2)$$

Here M is the mass of an atom and m the mass of the electron. ν_r is taken to be the maximum infra-red frequency and ν_v is the "violet" frequency which corresponds possibly to the frequency of the maximum selective photo-electric effect. This is equivalent to stating that the constraints acting on the valence electrons in the crystal lattice are equal to the constraints on the ions. Now to compute the constraint acting on an ion in the crystal lattice we have recourse to the familiar formula:

$$k^{1/2} = 2\pi M^{1/2}\nu_r \qquad (3)$$

where *k* is the constraint presumably acting on both valence electrons and ions alike in the crystal lattice; M is again the mass of the ion and ν_r the characteristic frequency. Table II contains values of *k* computed by means of this equation. The frequencies employed in these calculations are taken from a compilation by the author.[2] In the few cases where known they are those obtained from heat capacity measurements. For the remaining cases the data are those computed by the author by means of a modification of Lindemann's melting-point formula. Finally, the mass of the ion, M, was determined by dividing the atomic weight of the element by the atomic weight of hydrogen and then multiplying this quotient by the mass of the hydrogen atom, 1.660×10^{-24} gm.

[1] Haber: Verh. deutsch. physik. Ges., **13**, 1117 (1911).

[2] Scott: J. Phys. Chem., **30**, 577 (1926).

TABLE II

"Nearest Approach" of Ions and Values of k

	Li	Be	B	C
$k \times 10^4$	4.77	28.5 (36.6)	77.2	118.6*
$d_o \times 10^8$ cm.	3.03	2.28	(1.86)	1.54
	Na	Mg	Al	Si
$k \times 10^4$	2.21	8.49	12.1* (17.8)	29.1
$d_o \times 10^8$ cm.	4.00	3.22	2.860	2.35
	K	Ca	Sc	Ti
$k \times 10^4$	1.60	6.64	(14.1)	23.4
$d_o \times 10^8$ cm.	4.48	3.93	(3.41)	2.90
	Rb	Sr	Y	Zr
$k \times 10^4$	1.22	5.61	10.9	17.0
$d_o \times 10^8$ cm.	4.93	4.33	3.75	3.18
	Cs	Ba	La	Ce
$k \times 10^4$	0.88	5.24	8.4	10.6
$d_o \times 10^8$ cm.	5.34	4.52	4.0	3.64

The figures for *k* enclosed in brackets are the hypothetical ones obtained by the author in the above-mentioned communication; the values marked by an asterisk are based on frequencies obtained from heat capacity measurements; the value of *k* for cerium is the hypothetical one mentioned later in connection with Fig. 3. The lattice distances are taken from another paper by the author.[1] Here again hypothetical figures are enclosed in brackets. It is of interest to compare the value for diamond given in Table II with the figure computed by Smyth from refractive index measurements. The latter figure is 1.10×10^6, which is very close to the value given above.

In Fig. 3 are shown the results obtained when the constraint *k* acting on the valence electron is plotted against the constraint *f* acting on the outer group of electrons of the ion. A glance at this graph shows clearly that these two constraints are related by a simple linear function for each series of isoelectronic ions. A few features of the figure call for comment. The line representing the elements of the first period is drawn so that it passes through the point for diamond. In order to simplify the diagram, only the hypothetical values of *f* for yttrium and zirconium are given and they seem to be perfectly satisfactory. The points Be_1 and Al are obtained by using the hypothetical values of *k* given in Table II. The sole outstanding defect in this linear relationship is readily seen to be the point for silicon. Whether this deviation is real and is due to a faulty value for *f*, or whether it concerns some inherent property of the ionic forces cannot be decided at this time. Nor can any explanation be offered regarding the interpretation to be placed on the existence of the two focal points, a and b. It is a suggestive fact, however, that the value of *f* for the point a is precisely that of the carbon ion.

---

[1] Scott: J. Phys. Chem., **29**, 304 (1925).

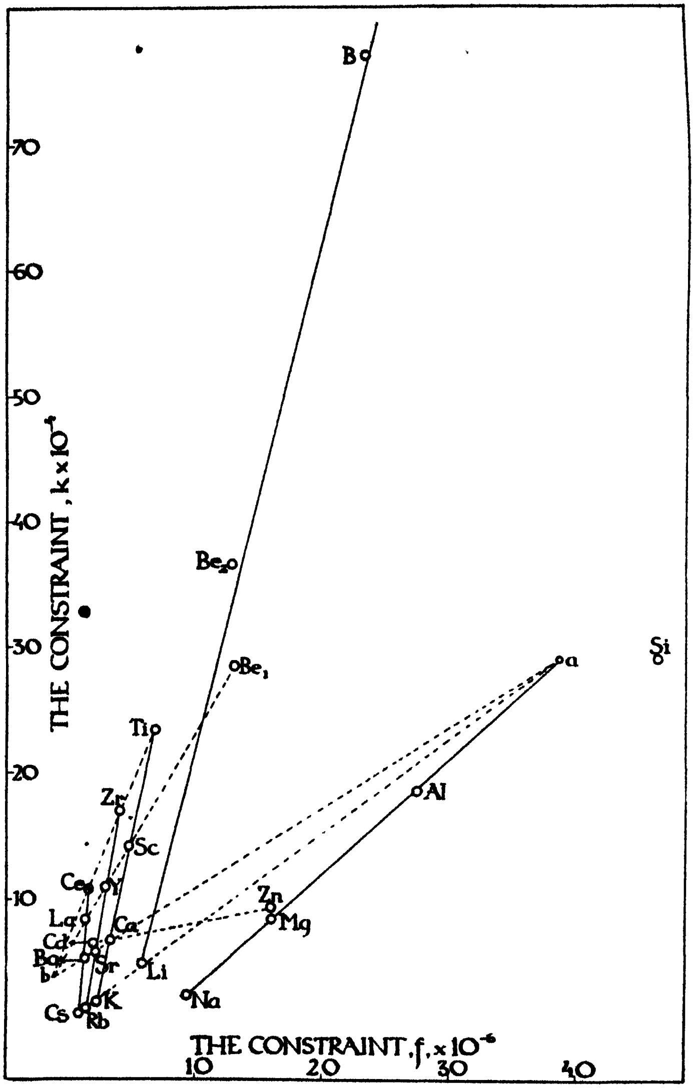


FIG. 3
Constraint on the Valence Electrons plotted against Constraint on Ionic Electrons.

The correct interpretation of the results of this figure may possibly yield valuable information for the understanding of the metallic state. The obvious deductions when combined with Haber's "square-root" rule enable us to propose a simple principle: Ions and electrons in the lattice of a metal are subject to the same forces and they are so assembled that this force, measured by their constraints, is linearly related to the constraints on the outer group of electrons of the ion when a series of iso-electronic ions is considered. If we may regard this principle as a necessary condition for the existence of a metallic crystal, we have some intimation as to the cause of the different orientations which iso-electronic ions take in the crystal lattice. For it is not easy to see how the type of lattice could be determined either by the structure or by the size of ions alone.

If the slopes of the lines in Fig. 3 are intrinsically characteristic of the structure of the ions—and this is practically the only possible assumption—, we are then in a position to make another instructive deduction: The valence electrons in the metallic state are to be regarded as still integral components of the atom and are subject to the same forces which control the electrons in the ions, namely, the so-called atomic forces. While this deduction is not very surprising, we have in it further confirmation of the evidence already accumulated against the classical theory of the "free" electron.

Verification of the conclusion that the valence electrons in the metallic state are subject to the same law of force as the more firmly bound electrons in the ions proper may be sought in still another direction. It has already been suggested that some definite relationship exists between the radius of domain of an ion and the constraints of the outer group of electrons on the grounds that they both depend ultimately on the same factors. Consequently, if our guiding idea is correct, we are justified in expecting a quite similar, if not identical, relationship to exist between the constraint k and the distance between the valence electron and the center of the ion, that is, the radius of the atom. Inasmuch as the data for the solid state are on the whole more reliable than those for the ions, it seems advisable to examine the former case first in order to ascertain what the relationship actually is.

The problem of analyzing this relationship brings us back to the original object of this study—the correspondence between the spatial attributes of the elements in the solid state and their chemical properties. In order to avoid any subsequent misunderstanding we are going to make the assumption that the square-root of the constraint, $k^{1/2}$, is essentially a measure of the "affinity" of metals for their electrons. Although an indisputable proof of this assumption cannot be given at this time, a fairly sound basis can be indicated in a rather roundabout manner. Equation (2) shows that the ultra-violet frequency of the electron is proportional to the square-root of the constraint, $k^{1/2}$. Lindemann[1] has demonstrated that this ultra-violet frequency is doubtless the frequency of the maximum selective photo-electric effect. Just at present, to be sure, there is some question as to the identity of this frequency and the threshold frequency of the normal photo-electric effect. But in any case, they must be closely associated. Consequently, we are reasonably safe in supposing that the product of this frequency by Planck's constant would, according to the well-known equation of Einstein for photo-electric emission, give us a measure of the intrinsic potential of a metal. And this is only an indirect way of saying that the square-root of the constraint which we will employ is substantially a measure of the forces of chemical "affinity".

---

[1] Lindemann: Ber.deutsch. physik. Ges., 13, 1107 (1911).

Now, a possible relationship between the constraint k and the lattice distance d_o (which, of course, is twice the radius of the atom according to our definition) has already been suggested by the author in the more recent communication of the two already cited. It may be expressed by the formula:

$$d_o = m\,k^{1/2} + n \qquad (4)$$

where m and n are constants for certain series of elements. To demonstrate its validity it will be advisable at this time to plot one variable against the other because nothing is known about the constraints involved. (See Fig. 4). For this purpose we shall require only the data contained in Table II. Where the data are reliable enough points for other elements than those represented in Table II have been offered (See Table III) in the hope that they may prove helpful towards an understanding of the characteristics of the graph. These additional data are from the same sources and have been computed in the same way as those contained in Table II.

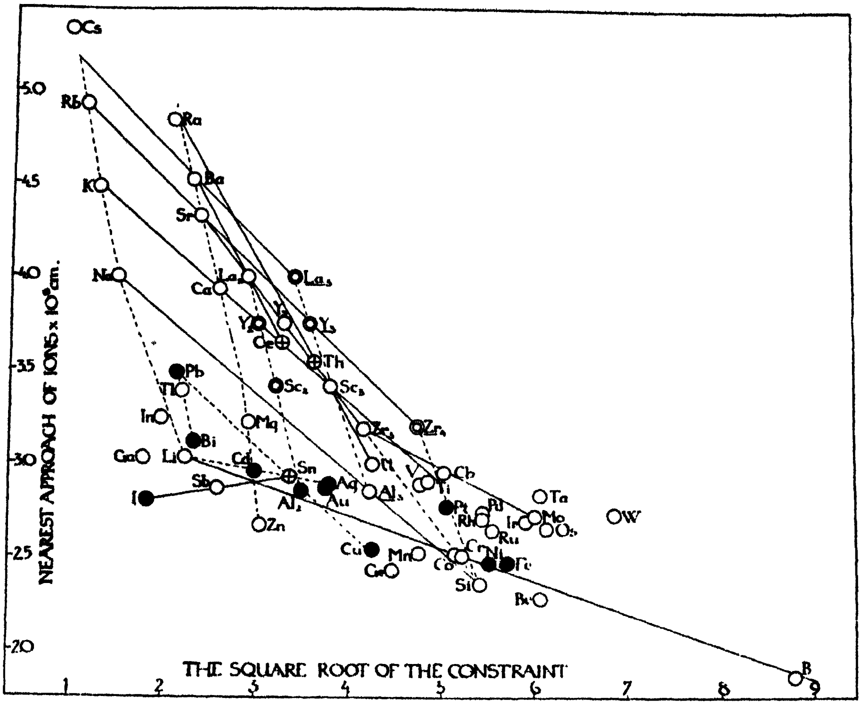


Fig. 4

Variation of Lattice Distance with Square Root of Constraint on Ions and Valence Electrons.

TABLE III

Additional Values of d_0 and k

Element	$k^{1/2}\times 10^2$	$d_0\times 10^8$ cm.	Element	$k^{1/2}\times 10^2$	$d_0\times 10^8$ cm.
Vanadium	4.75	2.89	Cadmium	2.98*	2.96
Chromium	5.21	2.508	Indium	1.97	3.24
Manganese	4.74	2.55	Antimony	(2.58)	2.87
Iron	5.70*	2.472	Tin	3.37*	
Cobalt	5.14	2.514	Iodine	1.82*	2.80
Nickel	5.50*	2.474	Tantalum	6.04	2.83
Copper	4.24*	2.543	Tungsten	6.84	2.732
Zinc	3.04	2.670	Osmium	6.11	2.66
Gallium	1.77	3.03	Iridium	5.88	2.690
Germanium	4.46	2.43	Platinum	4.04*	2.766
Columbium	5.00	2.95	Gold	3.74*	2.874
Molybdenum	5.98	2.720	Thallium	2.19	3.38
Rhuthenium	5.52	2.640	Lead	2.12*	3.479
Rhodium	5.42	2.700	Bismuth	2.32*	3.11
Palladium	5.42	2.729	Thorium		3.54
Silver	3.77*	2.884	Uranium	4.23	2.99

The asterisks and brackets possess here the same significance as in Table II.

The foregoing equation (4) has been arrived at by the elimination of the logarithmic term from the following two equations, which the author in the two previous communications already mentioned has shown to be reasonably accurate:

$$d_0 = a \ln (Z+e) + b \qquad 5a$$

$$k^{1/2} = a' \ln (Z+e) + b' \qquad 5b$$

Here Z is equal to the atomic number, and e the maximum number of valence electrons. The constants a, a′, b, and b′ are characteristic of certain series of ions. Obviously equation (4) will hold true only for those series of elements which are describable by both equation (5a) and equation (5b). Incidentally, the elimination of the logarithmic term furnishes a much more desirable condition for plotting, and the outcome may be used as a test of the validity of the two basic equations.

Because of the inherent uncertainties in the data, it was found necessary in constructing the graph to follow the above conditions with care. For this reason it is deemed advisable to list those series of elements for which we are justified in expecting equation (4) to hold. They are:

1. Li — Be — B — C
2. Na — Mg — Al — Si
3. K — Ca — Sc — Ti
4. Rb — Sr — Y — Zr
5. Cs — Ba — La —
6. K — Rb — Cs
7. Ca — Sr — Ba — Ra
8. Sc — Y — La

With this outline before us we may now proceed to examine the results in the individual series. The lines for Series 6, 7, and 8 are fully satisfactory, especially when due regard is paid to the source of the data. In Series 1 (the line passes through the point for carbon) the agreement is satisfactory. The same is true of Series 2, for almost the same discrepancy in d_0 for magnesium appears in plotting equation (5a); further, it should be observed that the point $\underline{Al}_3$ corresponds to the hypothetical constraint value already mentioned in connection with Fig. 3. In Series 3 the slight error in the constraint value for titanium is not unexpected. But it must be made clear that the constraint values for the points $\underline{Y}_3$ and $\underline{La}_3$ were chosen arbitrarily so as to comply with the stated conditions. This action is justifiable only on the grounds that the basic measurements for these constants are hardly reliable. But such an excuse is not available for the point Zr_4, even if we conjecture an error in the basic measurements due to a possible hafnium contamination. Because the constraint data are most susceptible to error, we could assume provisionally the lattice distance to be correct and then determine where the point for zirconium should come on the line through the points Rb and Sr. It comes at the point $\underline{Zr}_4$, which also lies, curiously, on a prolongation of the line through the points for silicon and titanium.

The difference between the constraint values of the points Zr_3 and $\underline{Zr}_4$ is far too great to be attributed to experimental error. Here we encounter the first unambiguous conflict with our conditions. The error must be sought in the validity of equation (5b). It will therefore be profitable to digress at this point and examine this relationship more closely. The situation is portrayed on a large scale in Fig. 5. Here the points Rb_1, Sr_2, Y_3, Zr_4, Cb_5, and Mo_2 are plotted according to the requirements of equation (5b). In the original communication dealing with this equation, a line was drawn through all the points except that for strontium, and the high value for this element was attributed to inaccurate melting point information. But a more careful study shows that this conjecture is highly improbable, and moreover, that if true it would completely disrupt the scheme of the graph, throwing the barium value out by too great an amount. There is an alternative method of plotting which deserves careful consideration. It is indicated by line A. The agreement, although only fair, is not unsatisfactory.

The possible interpretations of the break in this line, A, will become more definite after we have examined some further features of this graph. Heretofore we have found that the slope of the line representing equation (5b) was determined by the points for the first two elements in any period. Therefore let us draw a line through the points Rb and Sr_2, which we shall designate as line B, and which we shall refer to hereafter as the line of normal variation. Now, if we assume the number of valence electrons in zirconium to be 3 instead of 4, we get the point Zr_3 which, as is seen, falls precisely on line B. We might infer therefore that the constraint of zirconium is under the influence of only three valence electrons. But no such device will cause the actual constraint values of the other divergent elements to fall on line B, although certain regularities between the plotted points are apparent. On the other hand, if we ascribe to all the elements 3 valence electrons, we obtain the line C, in which the only marked defect is the questionable point for strontium. This result can scarcely be fortuitous. And yet, if it is not accidental, it means that in the term ln (Z+e), e is characteristic of this series of ions and that the constraint is subject only to the effect produced by changes in the atomic number. Without going into the matter more deeply, we may observe that in the line C the only point that is common to the original line, A, is the point Y_3, a fact that may be of real significance.

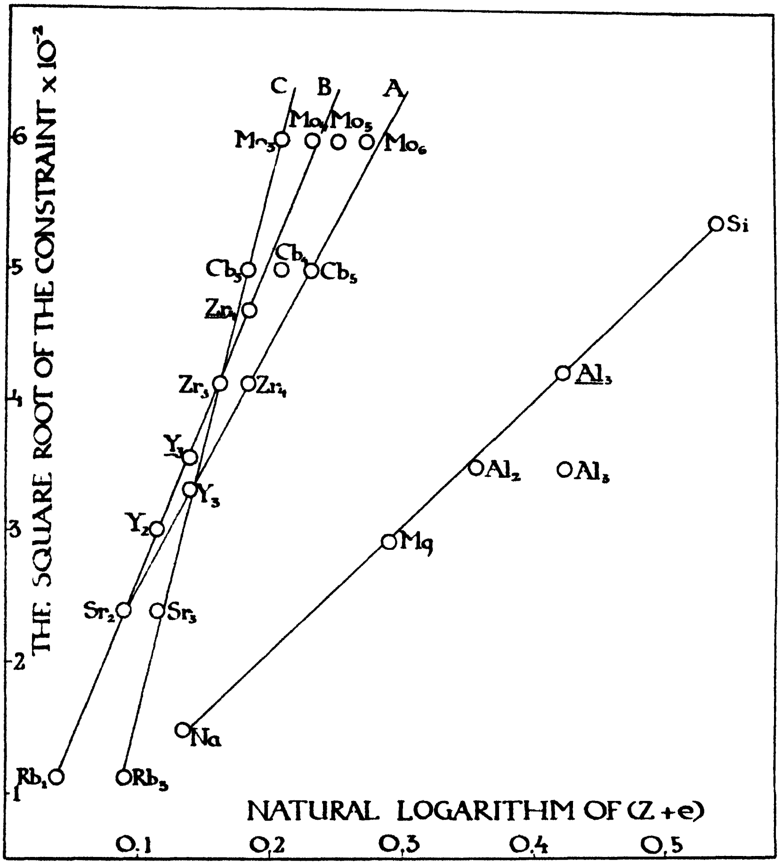


Fig. 5

Variation of $k^{\frac{1}{2}}$ with Function of Atomic Number and Number of Valence Electrons.

There is still another feature of this graph that should perhaps be pointed out. We may obtain the ideal hypothetical point $\underline{Zr}_4$ on the line B, and in view of the above conditions it is not surprising to find that this constraint figure corresponds exactly to that of point $\underline{Zr}_4$ shown in Fig. 4. And the same is true of the ideal point $\underline{Y}_3$. What is singular, however, is the fact that if we should obtain in the same way the hypothetical constraint values for columbium and molybdenum when e = 4; and if the points for these elements in Fig. 4 are plotted from these values, the points lie on the line through the points Rb, Sr, and $\underline{Zr}_4$. This is only another way of saying that the lattice distances of columbium and molybdenum behave as though they were controlled by four valence electrons while the constraints are subject to entirely different factors.

Similar and less qualified evidence of the same nature is afforded in the case of aluminium. In Fig. 5 the points for sodium, magnesium, aluminium, and silicon are plotted on the same scale as the other lines although there is no relation between them. Here the point marked Al_3 is based on the constraint figure calculated from the frequency value obtained from rather accurate heat capacity measurements. In the author's previous communication it was shown that this frequency value was much too low to comply with the type of variation exhibited by the other elements. Consequently a normal hypothetical quantity was determined by interpolation. Subsequently it was noted that the constraint calculated by means of this hypothetical frequency fell precisely on the line as indicated by the point $\underline{Al}_3$ in Fig. 5; but itwas also on the extension of the line through the points for scandium, yttrium, and lanthanum. Now it is clear that the point $\underline{Al}_3$ is analogous to the point $\underline{Zr}_4$ and is the hypothetical ideal point. To bring the actual constraint quantity on the line of normal variation it is only necessary to set $e = 2$; and the result is shown in Fig. 5 by the point Al_2. Here again we have a case where the lattice distance seems to be determined by the maximum number of valence electrons whereas the constraint is subject to the influence of a lesser number. What is most significant, however, is the fact that the divergence from the normal may be attributed to the effect of an integral number of electrons.

If the cases just cited are accepted as establishing a criterion for the number of valence electrons affecting the constraint, a number which is smaller than that controlling the lattice distance, we are at once faced with the difficulty of accounting for the "lost" electron or electrons as the case may be. But this difficulty is due to the lack of a suitable theory of the metallic state, a problem which is still unsolved. The following suggestions, however, may have some bearing on the difficulty in question.

Since we have already tentatively proposed to consider the behavior of the valence electrons in the metallic state to be somewhat analogous to their behavior in the atom, that is, to be subject to the same fundamental forces, it is only natural to turn first to atomic theory for information. Now, according to the Bohr theory, the Z-th electron in potassium, rubidium, and cesium skips the most probable quantum orbit and takes up a position in an orbit possessing less energy. This abnormality in filling up the orbits is ascribed to the effect of the ionic shell of electrons made up of $(Z-1)$ electrons about the nucleus. But this effect persists only for the next few additional electrons in each period when the concomitant increase in the nuclear charge offsets the disturbing influence of the ionic shell and compels the additional electrons to follow the normal rule. This break in the sequence is supposed to occur at scandium, yttrium, and lanthanum in the respective periods. In fact such a break has already been observed in Fig. 1. Hence, since in that figure we were dealing only with ions, we must attribute the break to a change in the forces which control the electrons in the outer group and which are inherent in the atom. Consequently, if the relation of the valence electrons to the ionic electrons is as intimate as we have supposed it to be, we may reasonably believe the abnormality encountered in zirconium to be the natural result of these changes in the atomic forces. An alternative view of the matter would be to assume certain fixed states for the valence electrons in the metallic state analogous to the orbits in the atom. Then the "effective" valence electrons may be assumed to be those in the outermost positions. But this conception of the situation also has many obstacles to overcome. Obviously it is too early to make a guess at the correct solution because we have no convincing hypothesis of the metallic state; yet these considerations will be of assistance in deciding the line of further analysis and in understanding the results.

Returning to the examination of Fig. 4, it is clear that if the above ideas have any bearing on the deviation of the point for zirconium, we must look for divergences in other cases. In fact the break in any sequence should make its first appearance, at least according to the first alternative, at scandium, yttrium, and lanthanum. In a word, a mistake was presumably made in establishing the conditions for the construction of Fig. 4. The revised conditions to be substituted for the similarly numbered conditions already given are:

3a. K – (Ca) – Sc – Ti
4a. Rb – (Sr) – Y – Zr
5a. Cs – (Ba) – La

The elements where a discontinuity is to be expected are enclosed in brackets. The problem now is to investigate this set of new conditions. Regarding Series 3a nothing definite can be stated because all the information about the critical element, scandium, is hypothetical. It may be observed, however, that the constraint value for the point Sc_3 is the one employed in making Fig. 3; but if we were to consider scandium to be analogous to aluminium, we should have the point Sc_2. Two singular relationships of this last point may be indicated: first, it lies on the line through the points Zr_3, Cb, and Mo; and second, a line through it and the point Ti most probably passes through the point for boron. More confidence may be had in discussing the other two series, for we have some actual measurements to go by. The conditions of Series 4a are fulfilled completely; moreover, a continuation of the line through the points of the last three elements passes clearly through the point for silicon. This relationship is doubtless associated with the fact that the point for thorium (obtained by plotting the value of d_o on the line through the points Ra and U) lies also on the line through the points Zr_3 and Si. In connection with the data for Series 5a, a statement should perhaps be made concerning the point for lanthanum. Apparently there is a similarity between the properties of this element and those of zirconium because the constraint value, if determined in a manner analogous to that used in Fig. 5, is identical for lines A and B when $e = 3$ and 2 respectively. Finally, as can be seen in Fig. 4, the points Sc_3, Y_3, and La_2 satisfy the conditions set down for Series 8.

While these results are consistent with our theoretical expectations, they are not decisive enough to permit a definite explanation of the cause of the break in the mode of variation of d_o with $k^{1/2}$. An examination of the conditions in the ions would be of great assistance towards an understanding of this difficulty. For it has already been suggested that a relationship analogous to equation (4) should hold for the radius of domain of the ion, *r*, and the constraint *f*. Such an expression would be:

$$r = c\, f^{1/2} + d \qquad (6)$$

In this equation c and d are constants analogous to m and n in equation (4). For the object in question the necessary data are wanting. But a representation of the data in Table I shows that equation (6) holds well within the limits of the accuracy of the data. The graph is not given, however, because it would not contribute especially to the discussion. The fact that equation (6) does hold approximately shows two things: first, why the square-root of the constraint was used in Figs. 1 and 2; and second, that the premise regarding the subjection of valence electrons to the same law of force as the ionic electrons is not entirely impossible.

Our results so far may now be viewed from the standpoint of our original problem, which concerned the relationship between the so-called chemical forces and the atomic volumes of the elements. If we consider the lattice distance so as to avoid the complications involved in the different types of lattice structure, and if we remember that $k^{1/2}$ is taken as a measure of the chemical "affinity", we may conclude that there are definite limitations to the correlation of these two factors. These limitations appear presumably because of certain divergences in the variation of the lattice distances and constraint forces in respect to the atomic forces. The normal rule which we assumed to describe the variation in the above cases is evidently modified in the latter case by some factor closely allied to the atomic forces. It is noteworthy, furthermore, that this modifying factor may be traced to the effect of valence electrons. Finally, it will be observed, the limitations just mentioned do not seriously vitiate the validity of the generalization that there is a relative correspondence between changes in spatial dimensions and chemical forces in the cases of those elements whose ions have structures similar to the inert gases.

While for this simple class of metals the variation of the lattice distance with the square-root of the constraint is rather clear, the case of the other metals is quite different. Such a result is now intelligible because of the greater variability in valence which these elements exhibit. The situation for many of the remaining elements is portrayed in Fig. 4. A word should perhaps be said concerning the point for tin. Since the lattice distance is unknown exactly, a line was drawn through the points for germanium and lead, and the proper constraint value was plotted on this line. The result seems to be peculiarly satisfactory. The line through the points for magnesium, zinc, and cadmium should be remarked especially because of the deductions of Bohr based on his interpretation of their spectra. In general, however, the behavior of different groups and periods of this class of metals is altogether different from that of the other type. Not only is this due to the greater possibilities of valence variation but also to the entirely different electronic structure of the ions. A feature that is somewhat puzzling, nevertheless, is the frequent interrelations shown by the points of these two groups of metals. A discussion of the characteristics of the second group must be postponed, however, until a subsequent communication in which the author hopes to show the underlying principle which is common to these two groups of metals and the non-metallic elements.

All the difficulties thus far encountered may conceivably be focussed in one general problem which concerns itself with the rôle played by the electrons in determining the constraint and the lattice distance in a metallic crystal. Whereas for a series of iso-electronic ions each valence electron has a definite and uniform effect upon the lattice distance, the effect produced on the constraint is not the same, even though it apparently follows a simple rule. If this divergence, however, were the only difficulty, it might possibly be overcome by making certain postulates: either that the effect of a valence electron on the lattice distance is invariable while the constraint is determined by the outermost electrons; or that the non-uniformity in the constraint variations is inherent in the structure of the atoms themselves. But actually this is not the sole difficulty. There is also the difficulty of accounting for the uniform effect these valence electrons have, no matter what the structure of the parent ion may be; witness the parallelism of the lines through the points of the elements of the first, second, and fourth groups. This effect becomes even more pronounced if we make one further hypothetical assumption. Let us assume that yttrium and lanthanum have two valence electrons such as we have concluded aluminium to have. To get the constraint values under this condition we have merely to interpolate on the normal line, B, in Fig. 5. The desired point is Y_2. The values for scandium and lanthanum can be obtained in the same way. These latter values are designated by the points Sc_2 and La_2 in Fig. 4. Now, when they are plotted in Fig. 4, it is seen that a line passes through them as well as through the corresponding point for aluminium, Al_2, and that the line is parallel to the other group lines.

There remains still unanswered the question why the lines for the different groups are straight lines like the lines for the different periods. But since they are straight lines and practically parallel, a situation which seems to be true also of the lines for the second, third, and fourth periods of elements, it is only natural to expect to find other interrelations of the points for the elements. But because no significance can be attached to these further relationships, a summary of them is omitted.

In the light of the evidence here presented it is at once apparent that the metallic state is exceedingly complex. To account for some of the results we could jump to the conclusion that there is a sort of equivalence in the effect of valence electrons and the effect of the various ionic groupings of electrons; but this would explain nothing. Or, we could outline the chain of evidence pointing unmistakably to the conclusion that the properties of the metallic state which we have discussed are definitely linked to the atomic forces. But this statement too would add little to the belief which is practically universal. These two ideas may be united by assuming that the valence electrons are not solely responsible for the similarity in properties of the different groups of elements. To restate this in another way, the inherent atomic forces which arrange the Z electrons of an atom in such a way that there are *e* valence electrons manifest themselves also in the similar nature of the ionic forces of all atoms with the same *e* electrons. In short, therefore, we may look for a similarity in ionic forces as well as for a similarity attributable to the presence of an equal number of valence electrons. In fact the frequently emphasized similarity in properties between elements of different valences such as beryllium and aluminium, and boron and silicon, shows that the valences are not the sole determining factors. Moreover, one could argue from the unique similarity in the ionic forces of the inert gases that this similarity does not vanish completely with uniform increases in the nuclear charge. Indeed, Figs. 1 and 2 are based on an assumption somewhat like this.

Despite the rather obscure character of the principle underlying the above considerations, it may be possible to see some confirmation of it in the following data. In Table IV are given the atomic volumes of a number of elements obtained by dividing the volume of one gram atom by Avogadro's number. We thus have a quantity which represents roughly the volume ascribable to a unit atom. The data employed to compute these volumes are taken from Landolt-Börnstein's Tabellen. Now, to determine the "electronic" volume, that is, the volume ascribable to each electron in an atom, assuming them all

TABLE IV

Atomic Volumes and "Electronic" Volumes

Element	Atomic Vol. $\times 10^{23}$ cc.	"Electronic" Vol. $\times 10^{24}$ cc.	Element	Atomic Vol. $\times 10^{23}$ cc.	"Electronic" Vol. $\times 10^{24}$ cc.
Lithium	2.16	5.39	Rubidium	9.26	2.44
Beryllium	0.81	1.63	Strontium	5.73	1.47
Boron*	0.73	1.22	Yttrium*	3.44	0.86
Carbon	0.57	0.81	Zirconium	2.36	0.58
Sodium	4.01	3.34	Columbium	1.98	0.47
Magnesium	2.32	1.78	Molybdenum	1.56	0.36
Aluminium	1.67	1.19	Caesium	11.80	2.11
Silicon	1.99	1.33	Barium	6.51	1.14
Potassium	7.53	3.77	Lanthanum	3.75	0.65
Calcium	4.29	2.04	Cerium	3.31	0.56
Scandium*	2.77	1.26	Lead	3.02	0.36
Titanium	1.78	0.77	Tantalum	2.08	0.28
Vanadium	1.87	0.78	Radium	7.83	0.88
Germanium	2.21	0.67	Thorium	3.50	0.31

*From a compilation by Sommerfeld: "Atomic Structure and Spectral Lines," page 99.

to be equally dispersed, use is made of a device of Bridgman.[1] Assume the nuclear charge to be of the same dimensions as the electrons. Then the "electronic" volume of an electron in an atom of atomic number Z is equal to the aforesaid atomic volume divided by the quantity $(Z+1)$. These figures are also included in Table IV. Although there is no physical significance to be attached to the "electronic" volumes, we may consider them to be a measure of the degree of packing of the electronic orbits in the atom when in the solid state.

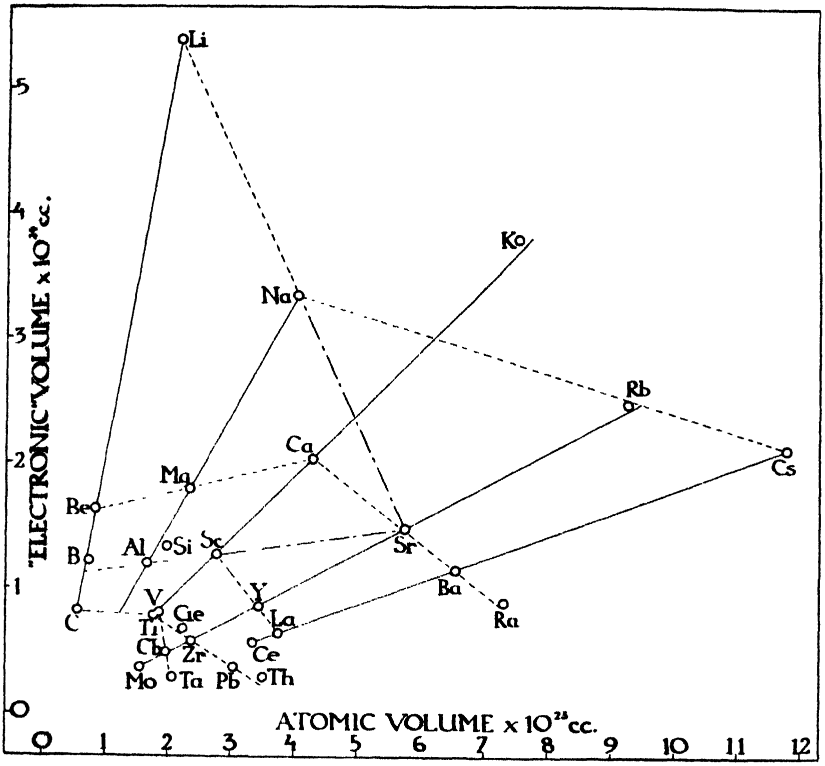


FIG. 6

"Electronic" Volumes of Elements plotted against Atomic Volumes.

In Fig. 6 we have the "electronic" volumes plotted against the atomic volumes. That the points for a series of iso-electronic ions should fall on an approximately straight line, is inherent in the scheme of the plotting, provided of course that the atomic volumes decrease regularly with increasing nuclear charge. For this reason discrepancies such as make their appearance with silicon and boron are no doubt to be attributed to uncertainties in the data rather than to some divergence from the normal behavior. The novel feature of this type of graph, however, is to be found in the lines representing the various groups. Regarding the grossly irregular position of the point for potassium, it may be observed that there is abundant evidence of the fact that this element has a particularly loose electronic structure and furthermore that in the solid state it lacks a definite crystalline state except possibly at very low temperatures. No further comment on this diagram will be made, first, because the precise significance of the terms employed is unknown at present; and second, because a possible qualitative interpretation has already been discussed.

---

[1] Bridgman: Phys. Rev., **27**, 68 (1926).

Summary

The present paper is to be regarded as a preliminary study of the relationship between the distance between ions in a crystal lattice of a metal and the chemical forces of that element. It is an attempt to find a more precise expression for the qualitative relationships which are known to exist between the chemical and physical properties of elements. The results may be summarized as follows: (a) The variation in d_o with $k^{1/2}$, which term is taken to represent the forces of chemical "affinity", may be expressed by a linear equation for certain series of ions; (b) the relationship between k and f for any series of iso-electronic ions is likewise linear and possibly represents a necessary condition for the existence of a crystal lattice; (c) the effect of changes in the nuclear charge upon f is found to be uniform for different series of iso-electronic ions. Deviations from (a) appear, however, in certain cases, and they are shown to correspond in some manner to the influence contributed by the valence electrons. In the data presented evidence has also been seen for the view that the valence electrons in a crystal are not "free" in the classical sense, but are still integral components of individual atoms. This concept constitutes, in fact, the guiding principle of this study. Moreover, considerations are advanced to show that the determining factors in group properties are to be sought in the characteristics of ions as well as in the number of valence electrons. And finally, a figure is presented portraying the surprising relationship which obtains between e "electronic" volumes and atomic volumes in metals.

In a subsequent paper the author hopes to extend these ideas and to discuss the application of these principles to the cases of non-polar elements and simple salts.

ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOALS I. A METHOD FOR THE PURIFICATION OF ADSORBENT CHARCOALS[1]

BY ELROY J. MILLER

Adsorbent charcoals because of their relatively great activity have been used perhaps more frequently than any other adsorbent in studies on adsorption from solution. Sometimes the assumption has been tacitly made that the material was essentially pure carbon and the role of the other constituents was ignored. It has been more generally recognized, however, that these adsorbents are extremely poorly defined substances and it is, therefore, not surprising that the results of these researches reported in the literature are largely discordant.

Many attempts have been made to purify these materials but they have been uniformly unsuccessful as far as any appreciable reduction of the inorganic content was concerned. The usual procedure was to extract the charcoals with concentrated acids, although occasionally fusion with alkali was attempted. Merck's blood charcoal seems to have been the favorite material for adsorption studies. While it is labelled, "Purified by Acids" it nevertheless contains in the neighborhood of 8 per cent of inorganic matter. Numerous investigators have sought to reduce the ash content further before use in their adsorption studies. Thus, for example, Freundlich and Losev[2] showed that the ash content of this material is not appreciably lowered by treatment with concentrated hydrochloric acid. They boiled the charcoal repeatedly with concentrated hydrochloric acid and then washed with hot distilled water and finally with conductivity water. The charcoal before treatment had an ash content of 7-8 per cent. After treatment the ash content was still 5-8 per cent.

Odén and Andersson[3] used essentially the same method and in addition subjected the charcoal to a final extraction with organic solvents.

Recently Firth and Watson[4] in a study of the catalytic decomposition of hydrogen peroxide solution by blood charcoal have carried out extensive studies on the removal of ash from blood charcoal by extraction with aqua regia. The charcoal before treatment gave on ignition 8.82 per cent of ash. Digestion with hot aqua regia for several days reduced the ash content to 7.30 per cent. After prolonged treatment for about a month with aqua regia the ash content was but little lowered. It still contained 6.32 per cent ash. Only by very prolonged treatment could the ash content be appreciably reduced below this figure. This drastic treatment resulted in the loss of a considerable portion of the charcoal and in some cases the whole of the charcoal passed into solution.

---

[1] Published as Journal Article No. 36 from the chemical laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director.

[2] Z. physik. Chem., **59**, 284 (1907).

[3] J. Phys. Chem., **25**, 311 (1921).

[4] Trans. Faraday Soc. **19**, 601 (1924).

In a previous paper[1] it was shown that boiling commercial sugar charcoal with concentrated hydrochloric acid reduced the ash content from 0.57 to 0.55 per cent a practically negligible amount, and this in spite of the fact that the ash remaining after burning off the carbon was largely iron and almost completely soluble in hydrochloric acid.

These illustrations from the literature on the subject are typical of the results obtained in efforts to purify adsorbent charcoals. Obviously, any method that could be used to purify these adsorbents should aid materially in furthering our knowledge of adsorption by eliminating the complications due to the uncertain action of the ash and should make the results of all investigators more easily reproducible and comparable. In previous publications[2] it has been shown that concordant and reproducible results can be obtained by the use of activated ash-free sugar charcoal.

It is the purpose of this paper to describe a method by which adsorbent charcoals of both animal and vegetable origin may readily be purified so that their ash content is reduced to a few hundredths or less of one per cent. The method has for its basis the use of hydrofluoric acid either alone or in mixtures with other suitable acids such as hydrochloric or sulfuric acids.

Method of Purification

The purification may be carried out in a number of ways but the following procedure has been found to be as satisfactory as any. The charcoal after thorough drying is ground to pass a 300-mesh sieve. It is then mixed in a platinum vessel with sufficient concentrated hydrofluoric acid to make a thin paste and warmed gently over a low flame (pilot light of a Bunsen burner is quite satisfactory) until most of the hydrofluoric acid has been driven off. When most of the hydrofluoric acid has been expelled the heating is increased to insure complete removal of hydrofluoric acid. The charcoal is next boiled with concentrated hydrochloric acid, diluted, and filtered through hardened filter paper in a Büchner funnel. This extraction with concentrated hydrochloric acid is repeated a second time after which the charcoal is washed by repeated boiling with distilled water until most of the hydrochloric acid has been removed. At this point the ash content of the charcoal has been reduced to a few tenths of a per cent, depending upon the kind and fineness of the charcoal and other factors. In order to reduce the ash content still further the charcoal is dried in an oven at 115° or higher and then ignited at a temperature of 900°-1200° in silica vessels from which air is excluded to prevent oxidation and loss of carbon. The above treatment with hydrofluoric acid and extractions with hydrochloric acid are repeated until the desired purity has been obtained. When the ash has been removed, the charcoal is ignited to drive off adsorbed acids and finally washed by boiling several times with a good grade of distilled water or preferably conductivity water and then dried. Ignition drives off practically all the adsorbed acids. A minute quantity of acid, however, remains even after the ignition. The amount is negligible for most purposes. It may be removed readily by boiling a suspension of the charcoal in conductivity water to which has been added approximately 1 cc. of 0.02 N sodium or potassium hydroxide per gram of charcoal. The excess alkali and the inorganic salt formed are quantitatively removed by boiling and filtering three or four times.[1]

---

[1] Bartell and Miller: J. Am. Chem. Soc., **44**, 1866 (1922).

[2] J. Am. Chem. Soc., **45**, 1106 (1923); **46**, 1150 (1924); **47**, 1270 (1925).

Results obtained in the Purification of Different Types of Charcoals

The method of purification described above seems to work equally well on all types of adsorbent charcoals. As examples of typical results obtained during the past several years in this laboratory in the purification of charcoals of animal, vegetable, and carbohydrate origin results for the following are presented: blood charcoal, Norit,[2] and activated sugar charcoal as representative of charcoals of animal, vegetable, and carbohydrate origin respectively. In Table I are given the results of ash determinations made on samples of charcoals taken after each of a series of treatments with hydrofluoric acid. Samples of charcoal weighing one to two grams each were ashed in platinum dishes over Meker burners or in an electric muffle.[3]

TABLE I

Ash Content of Charcoals after Successive Treatments with Concentrated Hydrofluoric Acid.

Kind of Charcoal	Number of Times treated with Hydrofluoric Acid	Per cent of Ash (Average of duplicate determinations)
Blood Charcoal (Lot A)	Before Treatment	8.39
	1	0 68
	2	0.13
	3	0.06
	4	0 06
	5	0.06
Norit	Before Treatment	6.47
	1	0.09
	2	0.04
	5	0.04
Activated Sugar Charcoal	Before Treatment	0.10
	1	0.00

---

[1] Miller: J. Am. Chem. Soc. 47, 1270 (1925).

[2] Tanner: Ind. & Eng. Chem. 17, 1191 (1925).

[3] *Note.* The ash remaining in the platinum dishes after burning off the carbon is usually largely insoluble in hot concentrated hydrochloric acid. The addition of a few drops of hydrofluoric acid dissolves the ash without injury to the dish or loss of platinum.

Inspection of the data in Table I reveals the fact that two or three extractions remove practically all of the inorganic matter from blood charcoal and that subsequent extractions do not reduce it further. Norit is somewhat more readily purified than blood charcoal but a minimum value is also reached, beyond which continued treatment is futile. The sample of sugar charcoal was prepared from recrystallized sugar and the introduction of the inorganic matter occurred after activation. This undoubtedly accounts for the fact that the ash content is reduced below one one hundredth of a per cent by the first extraction. In the case of animal and vegetable charcoals the small amounts of ash which cannot be removed are undoubtedly held within charcoal particles and they are, therefore, protected from the action of the acid. Further evidence substantiating this view will be found in Table II.

Experiments were conducted with the view of determining whether a mixture of hydrochloric and hydrofluoric acids might be substituted for the hydrofluoric acid alone, thereby eliminating the use of large quantities of the relatively expensive hydrofluoric acid. At the same time tests were made to see how much of a factor the fineness of division of the charcoal might be. Accordingly, samples of blood charcoal, one ground to pass a 300-mesh sieve, the other just as received, were treated as described in the above method with the exception that the charcoal was made up to a paste and heated with a mixture of approximately three parts of concentrated hydrochloric acid to one part of hydrofluoric acid. The data are presented in Table II. It is apparent that the purification of the charcoal can be effected by using a mixture of hydrochloric and hydrofluoric acids in which the proportion of

TABLE II

Ash Content of Charcoals after Successive Treatments with a Mixture of Concentrated Hydrochloric and Hydrofluoric Acids.

Kind of Charcoal	Number of Times treated	Per cent of Ash (Average of duplicate determinations)
Blood Charcoal (Lot B) Ground to pass 300-mesh sieve.	Before Treatment	7.85
	1	0.44
	2	0.12
	3	0.08
	4	0.06
	5	0.04
Blood Charcoal (Lot B) (Not ground)	Before Treatment	7.85
	1	0.71
	2	0.19
	3	0.15
	4	0.12
	5	0.13

hydrofluoric acid is relatively small. The purification is accomplished with practically the same number of treatments that are required with hydrofluoric acid alone.

It is also apparent that the fineness of division of the charcoal determines the amount of ash that cannot be removed on continued extraction. The coarser sample had a final ash content three times that of the one which had been ground to pass the 300 mesh sieve.

Use of Other Acids with Hydrofluoric

Mixtures of hydrofluoric and sulfuric acids were also tried and found to work fairly satisfactorily. They seemed to have no distinct advantage over the hydrofluoric-hydrochloric mixtures and, moreover, oxidation by the sulfuric acid with attendant loss of carbon was an undesirable possibility.

Removal of Nitrogen

Determination of the nitrogen in blood charcoal before and after purification showed that a marked reduction accompanied the removal of the ash. Prior to purification one sample of blood charcoal contained 0.59% nitrogen by the Kjeldahl method. After purification the nitrogen content was 0.26% It was found, however, that prolonged heating alone would remove nearly all of the nitrogen from the charcoal. One sample when heated in a closed silica crucible for 7 hours at approximately 1000° lost all but 0.06% of its nitrogen. Another sample heated for 3½ hours under the same conditions lost all but 0.15%. Since the nitrogen could be removed without reducing the ash content it seems that heating during the purification process rather than any action by the acid was responsible for the removal of the nitrogen from the charcoal.

Discussion

The method of purifying charcoals herein described effectively reduces the ash content to an insignificant amount. Previous attempts to purify adsorbent charcoals before use in adsorption studies by treatment with reagents such as concentrated hydrochloric and nitric acids, aqua regia, bromine, and chlorine have not met with success. Treatment with these reagents does not appreciably lower the ash content of the charcoal and in some cases in addition, results in the loss of a large proportion of the charcoal. The present method is free from these disadvantages and in addition does not appreciably affect the adsorbent power of the charcoal.

By means of this method adsorbent charcoals may be readily purified so that their ash content is practically the same as that of pure sugar charcoal. Data which have been obtained in adsorption studies with these purified charcoals are concordant and free from the contradictory results obtained with the unpurified materials. In every respect their adsorptive properties are identical with those previously reported for pure activated sugar charcoal. These results will shortly be submitted for publication.

Summary

(1) A method has been described for the purification of adsorbent charcoals.

(2) Data on the purification of animal, vegetable, and carbohydrate charcoals have been presented.

(3) By the use of this method it is possible to reduce the ash content of charcoals to a few hundredths or less of one per cent.

East Lansing,
Michigan.

ADSORPTION AND REACTION. I

The Setting of Plaster of Paris*

BY HARVEY A. NEVILLE

The setting of plaster of Paris is accelerated or retarded by various inorganic and organic substances which apparently act as catalysts in the reaction. The effect of this catalysis is such that a plaster which ordinarily sets in thirty-five minutes may be caused to set in five minutes by the addition of an accelerator, or delayed for an hour or more by a retarder. In attempting to account for this effect, Rohland[1] stated that any substance which increases the solubility of calcium sulfate will accelerate the setting of plaster of Paris, and that substances which decrease the solubility of calcium sulfate must retard the setting.

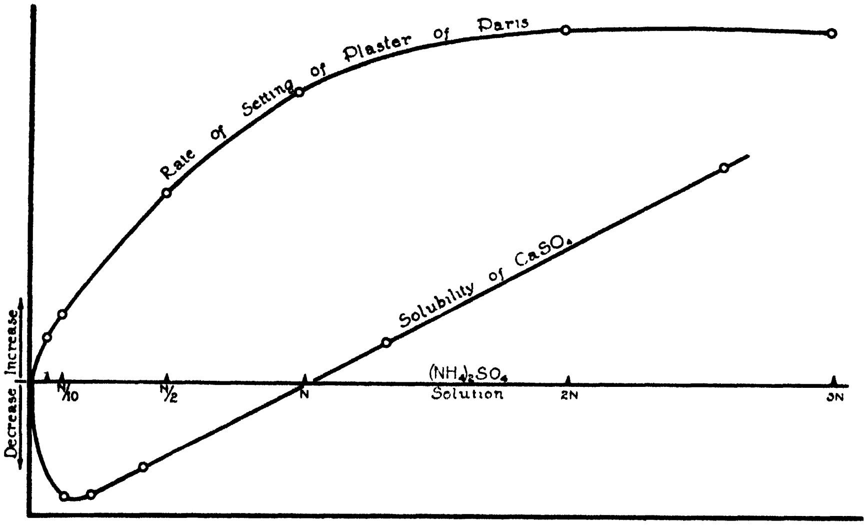


FIG. 1

The Rate of Setting of Plaster of Paris, and the Solubility of Calcium Sulfate as influenced by Ammonium Sulfate.

That this explanation is unsatisfactory is shown in Fig. 1, in which the effect of increasing concentration of ammonium sulfate on the rate of setting of plaster of Paris is compared with the effect of ammonium sulfate upon the solubility of calcium sulfate[2]. A complete absence of any relation is demonstrated. Furthermore, the solubility of calcium sulfate is *decreased* by small amounts of practically all soluble sulfates, yet these exert a marked accelerating effect upon the setting of plaster of Paris.

---

* Contribution from the Department of Chemistry of the University of Illinois.

[1] P. Rohland: Z. Elektrochem., **14**, 421 (1908).

[2] The solubility data are from Seidell's Tables of Solubilities; the data for rate of setting of plaster of Paris are from experiments described in this paper.

The explanation offered by Rohland was based upon the assumption that the mechanism of the setting of plaster of Paris is:

(a) The hemihydrate, $CaSO_4 . \frac{1}{2}H_2O$, dissolves in water to form a saturated solution.

(b) Hydration of the hemihydrate to the dihydrate, $CaSO_4 . 2H_2O$, occurs.

(c) Since the dihydrate is less soluble than the hemihydrate, the solution is now supersaturated and gypsum crystallizes, forming a compact mass of interlacing needle-shaped crystals.

If this were the true mechanism of the process, the effect of added substance would, no doubt, be as Rohland anticipated. More recent results, however, indicate that colloidal phenomena are concerned in the setting of plaster of Paris, as in the setting of lime-silica cements.

Cavazzi[1] and Traube[2], for independent reasons, suggested that the setting of plaster of Paris consisted in the formation of a gel which gradually changed into the needle-shaped crystals of gypsum. Traube studied the effect of accelerators upon the time of setting, measuring the time required for the plaster to attain that state of hardness where it was not displaced by a considerable pressure of his finger. He showed that the cations are the important factors in the acceleration, and concluded that their activity here agrees with the order in which they precipitate colloids from solution.

A kinetic method of studying the problem was developed by Wo. Ostwald and Wolski.[3] Their procedure was to measure, at intervals, the viscosity of dilute suspensions of plaster of Paris (2 to 5 per cent) and to consider the increase in viscosity an index of the progress of the action. The viscosity-time curves are found to be S-shaped; the viscosity rises slowly at first and then rapidly to a constant at its maximum value. By this method they were able to study the effect of varying the temperature, the concentration of the suspension, the age and fineness of the material, and the effect of added solutes. As a result of these experiments they conclude that the setting of plaster of Paris is a colloidal process, and they point out the similarity of its viscosity curves to those of gelatin.

Experimental Part

Method and Materials.—Since the hydration of plaster of Paris is an exothermal reaction, completely expressed,

$$CaSO_4 . \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O = CaSO_4 . 2H_2O + 3{,}900 \text{ calories},$$

it was thought that the reaction could best be followed thermometrically. By relating rise in temperature to time, a curve may be drawn which indicates the course of the reaction. By this method it is possible to use mixtures containing a much larger proportion of the solid than could be studied by the viscosity measurements, since the viscosity of mixtures which actually set quickly becomes infinite.

---

[1] Cavazzi: Gazz. chim. ital., **42** II, 626 (1912).

[2] Traube: Kolloid-Z., **25**, 62 (1919).

[3] Ostwald and Wolski: Kolloid-Z., **27**, 78 (1920).

A high-grade commercial plaster of Paris was used. In each experiment 40 g. of the plaster were used with 20 to 120 cc. of water or a solution. These materials were stirred for a definite length of time in a paraffined paper cup, the cup was then placed within another cup in a well insulated receptacle; a thermometer was placed in the mixture through a hole in the asbestos plate which covered the cup. The rise in temperature was noted at short intervals as the process of setting took place. The time-temperature curves showed a definite maximum which was reproducible within 30 seconds. The time corresponding to this peak was considered the setting time for the particular mixture, and comparative values for different mixtures were thus obtained.

TABLE I

40 g. of plaster of Paris stirred $\frac{1}{4}$ minute with 30 cc. of water or a solution. Time corresponding to maximum rise in temperature is given.

Reagent	Time in Minutes
Pure water	44
N. HCl	18
" $LiCl$	19
" $NaCl$	12
" NH_4Cl	10.5
" KCl	6
" KBr	6.5
" KI	8.5
" KNO_3	7
" K_2SO_4	7.5
" Na_2SO_4	12.5
" $(NH_4)_2SO_4$	6
" $CuSO_4$	12
" $MgSO_4$	20
" $ZnSO_4$	12
" $Al_2(SO_4)_3$	25
Saturated $CaSO_4$	44
" H_3BO_3	63
" $NaCl$	180
" $Na_2B_4O_7$	3 days.

Results.—In Fig. 2 are illustrated the reaction curves for a mixture of 40 g. of plaster of Paris with 30 cc. of water, for a similar mixture accelerated by potassium sulfate, and for one retarded by glycerine. When plaster of Paris and water, in the proportions noted, are thoroughly stirred for a short time, a thin paste or cream is formed which can easily be poured into molds. There is a slight rise in temperature at this point—usually less than one degree—due to the heat of wetting or adsorption, sometimes referred to as the Pouillet effect. After standing about six minutes, however, the mixture can no longer be poured. When 40 g. of the plaster are mixed with 30 cc. of normal K_2SO_4 solution the materials cannot be stirred for longer than one-half minute, for the mixture is stiff at the end of that period. Prolonged stirring shortens the time required for setting, hence a half-minute uniform stirring was adopted for the experiments. The point -S- on the curves corresponds to the initial set stage. At this point the plaster is perfectly rigid, resists indentation, and has a dry appearance. The broken-line curve represents the volume change, with time, of a mixture of 40 g. of plaster of Paris and 30 cc. of water, corresponding to the temperature-time curve labelled "Water".

The effect of various substances in modifying the rate of setting of plaster of Paris is shown in Table I. The time noted corresponds to the maximum temperature reached, or final set. The initial set, indicated by the point -S- on the curves in Fig. 2, was affected proportionately in each case. In addition, it was observed that the setting was faster when the original temperature of the water was higher; and that it was slower when larger proportions of water were used.

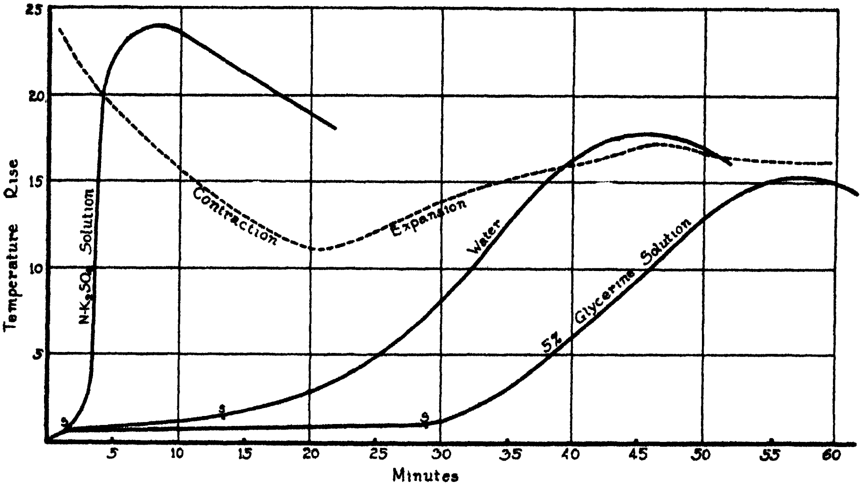


FIG. 2

Time—Temperature Curves for the Setting of Plaster of Paris. Broken Line = Volume Change for Water—Plaster.

Discussion

From a consideration of the curves in Fig. 2, it is apparent that there are two stages in the setting process. Since the point -S- is on the flat part of the curve, before the evolution of heat has begun, the hydration of plaster of Paris to form gypsum cannot have occurred to any appreciable extent. It follows, therefore, that the initial hardening of the mixture is not due to chemical combination with water. The facts point rather to the formation of a gel or adsorption complex in which only physical or secondary chemical forces are concerned. The volume-time curve in Fig. 2 confirms this conclusion. It indicates clearly that two processes are involved: adsorption of water, accompanied by a contraction in volume; formation of gypsum crystals from the adsorption complex, accompanied by an expansion. The final volume is less than the sum of the original volumes of the materials by about seven per cent, as can be calculated from the respective densities of the substances concerned.

Ordinary plaster of Paris, made by the partial dehydration of gypsum, must have a very incomplete crystal structure with residual crystal forces and an enormous surface. It is to be expected that this type of material would have very strong adsorptive forces. It is reported that a crystalline form of $CaSO_4 . \frac{1}{2}H_2O$, obtained by prolonged boiling of gypsum with water, does not set as does plaster of Paris.[1] It is likewise to be expected that lime, made by the calcination of calcium carbonate, would have a porous structure like that of plaster of Paris. Hence it is of interest to note that Kohlschütter and Walther[2] concluded that an intermediate colloidal state first occurs when lime is mixed with water to form a true solution of calcium hydroxide.

The forces of adsorption having brought the plaster of Paris and water into the sphere of chemical action, chemical forces effect a reaction between the two substances to form gypsum, crystals of which grow throughout the material. An approximate determination of the heat evolved indicates that practically all of the hemihydrate has reacted at the time corresponding to the maximum temperature reached.

It is apparent that the reaction is very susceptible to catalysis. A measure of this, as given in Table I, brings out certain interesting relations. As pointed out by Traube, the accelerating effect of a salt is due to the cation, controlled to some extent by the anion which is present. It is seen that, in general, the activity of the cation increases with its weight. Thus, with the monovalent ions, $K > NH_4 > Na > Li$. Here the ammonium ion has a greater activity than the sodium ion although its weight is less. Among the divalent cations the same relationship holds: $Cu > Mg$, and $Zn = Cu$, since the latter pair are practically equivalent in weight.

The anions exert a minor influence, apparently limiting to some extent the activity of the cation. Considered as retarders, the order of the monovalent anions is: $I > NO_3 > Br > Cl$. Here the nitrate ion shows a greater retarding effect than the bromide ion, although the latter is heavier. Perhaps the size of the nitrate and ammonium ions may compensate for their lighter weight.

The relations outlined are certainly suggestive of colloidal phenomena. The order of the alkali metals in accelerating the setting of plaster of Paris is the same as that observed in the coagulation of a negative colloid of the suspensoid type. The order of the anions is likewise normal in that sense. An exception is shown in the order $K > Mg > Al$, since the polyvalent ions are usually the more active in colloidal processes. The exact role of the accelerating ions is not clear, although it is evidently twofold. That is, the adsorption of water to form the gel is accelerated by these ions; then the chemical reaction between the hemihydrate and water is catalyzed. The substances which retard the setting of plaster of Paris—for example, borax and saturated sodium chloride solution—do so because they prevent the formation of the gel. Here the setting process is probably one of solution, hydration and crystallization; and the set mass which results after this slow process is composed of large crystals, is crumbly and without strength.

---

[1] W. A. Davis: J. Soc. Chem. Ind., **26**, 727 (1907).

[2] Kohlschütter and Walther: Z. Elektrochem., **25**, 159 (1919).

The results of Ostwald and Wolski[1] from viscosity measurements of dilute suspensions of plaster of Paris indicate the colloidal nature of the mixture by analogy to properties of known colloids. We are not able, however, to discover from their data the point at which the dihydrate is formed or if it is formed at all. The thermometric method shows definitely the two stages in the setting. Ostwald and Wolski emphasize the importance of the maximum viscosity attained in each case and the effect of varying conditions upon this maximum. It would seem, rather, that the rate of increase in viscosity is of more importance, since it probably indicates the rate of setting. If the slope of each viscosity-time curve constructed by those authors is considered the *rate of viscosity increase*, then varying conditions affect this factor just as they do the *rate of setting* of plaster of Paris, studied by the method described here. It is of interest to note that it was found in both of the investigations that it made no difference if a saturated solution of gypsum was used in place of pure water.

Part of the experimental work for this paper was performed by Victor L. Soderberg, to whom acknowledgement is hereby made.

Summary

1. The setting of plaster of Paris occurs in two stages. This is shown by relating rise in temperature to time and also by measuring the change in volume with time.

2. The two stages of the process are: (a) adsorption, accompanied by a contraction in volume and a slight heat effect, whereby the two reactants are brought into chemical contact; (b) a resulting exothermic chemical reaction between the adsorbed liquid and the adsorbent, with an increase in volume.

3. The relative effectiveness of various substances in accelerating the setting is shown. This effect is not due to increased solubility of calcium sulfate, but results from the colloidal nature of the mixture of plaster of Paris and water.

Urbana,
Illinois

---

[1] Ostwald and Wolski: loc. cit.

Indian Agricultural Research Institute (Pusa)
LIBRARY, NEW DELHI-110012

This book can be issued on or before......................

Return Date	Return Date